UNIVERSITA' DEGLI STUDI DI NAPOLI FEDERICO II
CENTRO INTERDIPARTIMENTALE DI RICERCA "AMBIENTE"
(C.I.R.AM.)

PhD in
ANALISI DEI SISTEMI AMBIENTALI

Curriculum
SCIENZA DELLA TERRA E DELLA VITA
IN ARCHEOLOGIA E SVILUPPO SOSTENIBILE

XXII CICLO

DISTRIBUTION AND SPECIATION OF POTENTIALLY TOXIC METALS IN THE ABANDONED UPPER MOULOUYA MINING DISTRICT (MOROCCO)

PIETRO IAVAZZO

Tutors
Prof. Paola Adamo
Prof. Daniela Ducci
Prof. Maria Boni
Dr. Stephen Hillier

Coordinatore
Prof. Filippo Barattolo

a.y. 2006-2009

CONTENTS

CHAPTER 1

FOREWORD

1.1 PTMs contamination

The role of man in the biosphere has been so important recently that it has become necessary to distinguish the anthroposphere, the sphere of man's settlement and activity, which can be applied to any part of the biosphere that has been changed under an influence of technical civilization. While geological and biological alterations of the earth's surface have been very slow, changes introduced by man have accumulated extremely quickly in recent years (Kabata-Pendias and Pendias, 2001).

Environmental pollution, especially by chemicals, is one of the most effective factors in the destruction of the biosphere components. Among all chemical components, potentially toxic metals (PTMs) are believed to be of a specific ecological, biological and health significance. In soils their forms are strongly determined by their origin and history. Although native metals are frequently in highly immobile forms, anthropogenic forms are often more reactive and thus are more available to plants. The soil is a dynamic system and any changes in environmental conditions, whether natural or anthropogenic, can alter the forms of PTMs, thereby affecting their behaviour in soil. The main controlling factors include degradation of organic compounds, change of pH, redox potential and ionic strength of the soil solution, solid and solution components and their relative concentrations and affinities for an element, and time (McLean and Bledsoe, 1992; Misra et al. 1994; Alloway, 1995; Herreweghe et al. 2002; Jung et al. 2002; Liu et al. 2003; Tahiri et al. 2005).

The term PTMs includes essential (e.g., Cu, Mn, Se, Zn, Co) and nonessential (e.g., As, Hg, Cd, Pb) elements. The elements essential to healthy functioning and reproduction of microorganism, plants and animals are required in low concentrations and are also called micronutrients, but at high concentrations they may cause direct toxicity or reproductive effects for plants, animals, and humans (Bolan and Duraisamy, 2003). Some elements are also non-essential and even low concentrations of these elements in the environment can cause toxicity to both plants and animals (Alloway, 1995).

PTMs contamination is widespread, as they are non-biodegradable and therefore persist for long periods in aquatic as well as terrestrial environments (Kabata-Pendias and Pendias, 2001;

Grandjean and Landrigan, 2006). It is generally accepted that the distribution, mobility, bioavailability and toxicity of PTMs in soil depend not simply on their total concentrations but, critically, on their forms (Morgan and Stumm, 1995). These may be soluble, readily exchangeable, complexed with organic matter, or hydrus oxides, substituted in stoichiometric compounds or occluded in mineral structures (Ritchie and Sposito, 2002).

PTMs can be retained by soils and/or mobilized to soil solution by biological and chemical mechanisms with a potential impact on human health (contamination of drinking water supplies and agricultural crops and input into the food chain) (Giuliano et al., 2007; Ajmone-Marsan et al., 2008; El Khalil et al., 2008).

The fate and transfer of metals are complex and depend on the transport process involved, on the mineralogy of eroded particles and on soil and sediment properties (Krishnamurti and Naidu, 2003; Razo et al., 2004; D'Amore et al., 2005). The biogeochemical processes that control metal mobility and bioavailability include sorption on mineral and organic surfaces, dissolution, (bio-)mineralization, redox processes, complexation by biogenic or non-biogenic ligands and uptake by the biota (Kraemer and Hering, 2004). These processes could determine the metal speciation in the environment and therefore, their bioavailability and toxicity.

1.2 Speciation in risk assessment

The term "derelict" is commonly used to describe land that has been spoiled by industrial operations (e.g. the extraction of minerals) or as a result of general neglect and so is incapable of beneficial use without some form of remediation. In many countries some of the worst dereliction is associated with old mineral workings. These may take the form of old spoil heaps and tailings ponds and associated buildings and structures which may include mine shafts, or of open pits and quarries (Bell and Genske, 2000). According to Genske and Thein (1994), the key to effective rehabilitation of derelict land involves the harmonized management of ground investigation, risk assessment and cleanup strategies. Contamination can take many forms and can be variable in its nature across a site and each site has its own characteristics. Hazard implies a degree of risk, but the degree of risk varies according to what is being risked. It depends, for example, upon the mobility of the contaminant(s) within the ground and different types of soils have different degrees of reactivity to compounds that are introduced. Also, it is influenced by the future use of a site.

Remediation technologies of PTMs contaminated environments are complex and may involve a combination of physical, chemical and biological methodologies. These have the purpose of immobilizing, containing, isolating, extracting and/or disposing of PTMs (Siegel, 2002).

Risk management based only on the total content of PTMs in soil is generally used as the first reference indicator for comparing pollution level with legislative limits and might be useful to detect any net change due to different possible phenomena, such as erosion and leaching to groundwater, in order to minimize the risks assuming that pollutants transferring to water resources or biota increase with contamination level. Nevertheless total metal content analysis is not enough to evaluate the influence of each element in the potential ecosystem pollution and gives no idea of the extent to which elements are really transferable or bioavailable (Morin et al., 1999; Pagnanelli et al, 2004); the natural occurrence of toxic elements in soils, especially in disused mining areas, requires further analyses to detect mobilisation due to erosion and leaching to groundwater (Giuliano et al., 2007).

For a correct assessment of risk/toxicity (according to PTMs' content and availability) of a polluted soil and to predict its decrease after application of remediation techniques, it is crucial to establish the speciation, mobility and biogeochemistry of the contaminants (Wennrich et al., 2004).

According to Ure and Davidson (2002), the term "speciation" identifies and quantifies metal pools present in soils. Speciation science seeks to characterize the various forms in which PTMs occur in soil or, at least, the main metal pools present in soil. Understanding speciation is important for assessing the potential of soil to supply micronutrients for plant growth or to contain toxic quantities of PTMs, and for determining amelioration procedures for soils at risk of causing the PTMs' contamination of waterways.

The residence time of an element in a soil depends on the mobility of its predominant forms: not all metals are equally reactive, toxic or available to biota and the free ion form of the metal seems to be the most available and toxic. Because of the dependence of metal mobility on the interaction of metal with soil, several sequential procedures have been developed to selectively remove metals from the different geochemical forms (Lake et al., 1984; Allen, 1997; Song et al., 1998).

PTMs' speciation in soil can be achieved using either direct or indirect analytical methods. Direct methods, mainly non destructive, are usually qualitative and often not sensitive enough to detect forms present in small amounts; furthermore, they are more sophisticated than chemical methods and need a high level of specialization to be routinely included in metal speciation studies.

More widely applied to determine the potential, plant and human bioavailability are the methods of PTMs' speciation which involve selective chemical extractions techniques. Estimation of the plant- or human-available element content of soil using single chemical extractants is an example of functionally defined speciation, in which the function is plant or human availability. One approach to this problem is to apply various chemical extractants, either singularly or sequentially in order to assess the forms, or at least the main pools, in which metal contaminants occur in solid samples (e.g. Ure and Davidson, 2002; Adamo and Zampella, 2008). These procedures are all based on the general principle of reacting a soil sample with chemical extractants classified according to their ability to release elements from specific soil phases and characterized by increasing strength.

Partial or sequential extraction methods are among the oldest and most commonly used methods of chemical partitioning of environmental solid samples. Perhaps the simplest and most standardized sequential extraction method was proposed by the European Community Bureau of Reference (BCR) (Ure et al., 1993). These techniques are easy to apply, inexpensive, and require little data analysis. However, it is vitally important to realize that the original work on sequential extraction was performed on sediment materials with trace metal concentrations (Tessier et al., 1979). Since then, many researchers have adapted these methods to study anthropogenic metal contamination and to predict or estimate bioavailability of various metal forms. The idea behind these extraction methods is based on the assumption that a particular extractant is phase or retention mode specific in its chemical attack on a mixture of forms. However, it is now widely recognized that the forms determined by chemical extractions are inevitably operationally defined (Hillier et al., 2001; Ure and Davidson, 2002).

These procedures present a series of different problems, which play a role in determining the success of a given extraction procedure, such as the low reproducibility especially with large particles and encapsulated pollutants (Dahlin et al., 2002a), the error propagations (Koeckritz et al., 2001), the strong influence of operative conditions (Koeckritz et al., 2001; Ngiam and Lim, 2001), the chemical properties and the effective selectivity of the extracting reagents (Nirel and Morel, 1990) and the re-adsorption of metals during extraction (Rendell et al., 1980).

Further considerations apply if the extraction procedure is a sequential scheme for determining a fractionation pattern for a given soil or sediment sample. These include: (i) the sequence of steps, (ii) matrix effects (cross contamination and re-adsorption), and (iii) heterogeneity and physical associations of the solid components. Lastly, sample procurement,

handling, storage, and preparation all affect the results in a crucial way (D'Amore et al., 2005).

As a consequence, sequential extraction procedures cannot be used as stand-alone evaluations to identify the actual form of metals in soils and should be accompanied by deeper experimental investigations and solid matrix characterization (Dahlin et al., 2002a, b). However, sequential extractions can be useful to have an operational classification of metals in different geochemical fractions (Pagnanelli et al, 2004). Therefore, a complementary use of the chemical and mineralogical approaches may provide a more realistic picture of the actual forms of PTMs in solid matrices (Adamo et al., 1996; Venditti et al., 2000a, b; Adamo et al., 2002; Adamo et al., 2003; Hillier et al., 2003; Kirpichtchikova et al., 2006).

1.3 PTMs in mining activities

There are a multitude of anthropogenic emissions in the environment. Man's perturbation of nature's slowly occurring life cycle of metals includes (i) the extraction, smelting, and processing of metal bearing ores into products, (ii) the distribution and use of these products by industry and consumers, and (iii) the return of these metals in a concentrated form to the natural environment through disposal of processing wastes and the discard of spent products.

Some soils contain high concentrations of metals from geochemical sources (Adriano, 1986), while others are contaminated by metals from these anthropogenic activities which have increased the prevalence and occurrence of PTMs contamination at the Earth's surface (Osher et al., 2006). Although metal mining can bring much economic prosperity, large areas of industrial dereliction often result once mining has ceased. This dereliction includes a legacy of abandoned tips, which contain the waste products of both mining and ore processing operations; the waste is commonly disposed on the earth's surface in piles of rock called tailings or spoil piles. Such materials are often a major source of PTMs pollution in the local environment due to discharge and dispersion into nearby agricultural soils, food crops and stream systems (groundwater and surface water) (Tordoff et al., 2000; Jung, 2001). Many research studies are devoted to element migration in solid waste and adjoining soil (De Vos et al., 1995; Seal and Hammarstrom, 2003), surface waters (Shallari et al., 1998; Tsareva et al., 1999), ground deposits (Task et al., 1996; Gupta and Karuppiah, 1996) and other environmental components (e.g. atmosphere as metal-enriched dust) (Callender E., 2003).

Mining is one of the industrial activities that causes the greatest and most persistent alterations in nature (Passariello et al., 2002). This activity affects relatively small areas, but could have a significant impact on the environment representing a potential danger to the health of human populations residing in the vicinity of these mining areas. The pre-existing ecosystems in mining areas become subjected to such disturbance that the most common consequences is their disappearance; the territories in the vicinity are very vulnerable and usually very much affected (Marqués et al., 2001). Following mine closure, the tailings are disposed onto surrounding soils, leading to their exposure to environmental factors (El Khalil et al., 2008). The impact of mining activity on a given site is controlled by several factors, including the climate, mining methods, geological conditions, degree of mineralization of the tailings and whether the mine is active or abandoned (Johnson et al., 2000; Bell et al., 2001).

Several chemical contamination cases have been described in former mining areas, where significant amounts of various elements were mobilized by weathering and by leaching from abandoned mining wastes (Hartwell et al., 1983; Abrahams et al., 1987; Hamilton, 2000); according to Merrington and Alloway (1994), over 100 years after the closure of some Pb-Zn mines of Wales, considerable amounts of metals are still being transferred off-site.

In semi-arid areas, the dispersion of soluble and particulate metals is often enhanced because soils are typically scarcely vegetated (Navarro et al., 2008). These areas have severe erosion problems caused by wind and water runoff in which soil and mine spoil texture, landscape topography and regional microclimate play an important role (Adriano 1986; Johnson et al., 1994; van Geen et al., 1999; Querol et al., 2000; Chopin et al., 2003; Boularbah et al. 2006a,b).

There is an obvious need to restore these disturbed habitats, although they have usually been altered to such a degree that they can only be partially restored, land reclamation or rehabilitation being the remaining alternatives (NAS, 1992). Environmental managers should concern themselves with a detailed knowledge of all potentially mobile and toxic metals within the economic, and gangue minerals, and the waste rocks and overburden associated with the ore body (Clark, 2001).

1.4 Mining activity in Morocco

The mining history of Morocco can thus be summarized by the history of lead prospecting within the country (Bouabdli et al., 2005). Morocco has been the most important lead producer in north Africa since Roman times (Emberger, 1965). Mining activity started in Morocco in the 9th century. Strong mining activity resumed in the 1970s and has been maintained since that time, with lead still being the main metal produced. In 1980 its production reached about 170,000 tons of concentrated lead, which corresponds to 3.5% of the world's production (Wadjinni, 1998).

Mainly the southern region has large areas covered by metalliferous sites some of which are being exploited while others have been abandoned (Chronicle of mineral research and exploration, 1998); these sites are concentrated in the region of Marrakech, Ouarzazate and in the north of the Anti-Atlas mountains (Abarro et al., 1998; Eddebbi et al., 1998).

The mining sector plays an important role in Morocco's economy. In 2001, mining products accounted for close to 13% of total exports. The sector employs 37445 people. Morocco is the leading exporter and the world's third largest producer of crude phosphate, and the second largest exporter of solid fertilizer. Baritin, zinc, lead, cobalt, fluorite, bentonite, and smectite clays are some of Morocco's other important mining products.

The mining legislation in effect is to be found in the Dahir of 16 April 1951 containing the mining regulations, as amended, together with the implementing texts. The Government's strategy in this sector covers all mining activities (upstream and downstream). Its aim is to promote geological and mining potential, develop prospecting, diversify outlets, create a climate favourable to partnerships, and adopt legal and fiscal incentives.

This decree does not provide a regulation concerning the environmental safeguard from risks due to the mining exploitation at the present (working mines) and in the past (abandoned mines) (El Hachimi, 2006).

1.5 The Upper Moulouya mining district

The Moulouya River is the largest river in Morocco (length: 520 km), draining approximately 53500 km^2 in eastern Morocco between 32° – 35° N and 2° – 6° W. It rises in the Atlas Mountains at an altitude of 1770 m and flows into the Mediterranean Sea.

Due to the presence of mountainous areas (Rif, Middle and High Atlas), the Moulouya River basin is characterized by variable relief. The river basin also contains high plateaus (the Horsts chain) and low plains (the Missour-Outat El Haj and the Taourirte-Guercif basins). This large area can thus be subdivided into three zones designated by the upper, middle and lower Moulouya basins (Bouabdli et al., 2005). Topographically, about 3% of the drainage basin is mountainous (altitude > 2500 m), 15% is hilly (1500 – 2500 m), 71% extends on foothills and a plateau region (500 – 1500 m) and 11% consists of plains and valleys. The slope of the stream gradually decreases from about 0.56% in the upper part of the basin, to 0.32% in the middle part and 0.19% in the lower floodplain. The bedrock consists predominantly (97%) of sedimentary rocks (limestones, marls, sandstones, conglomerates, etc.); while crystalline and metamorphic rocks crop out only over 3% of the basin area. The main human activities in the Moulouya basin are agriculture (138000 km^2 of irrigated lands), industry, mining and grazing. Agriculture is developed mainly in the lower Moulouya, where the soil is fertile and water abundant. The main crops grown are cereals, vegetables, and sugar beet. In the more arid zones, the land is used mainly for livestock grazing. Forests are developed on the slopes of the Atlas and on the Beni Znassen mountains (Snoussi et al., 2002).

The site of interest, the High Moulouya valley, also known as the Upper Moulouya lead district, corresponds to the south-western region of the Oranaise Meseta that is bounded by the High Atlas on the southeast and by the Middle Atlas on the northwest (Piqué and Michard, 1989). The region is composed of two separate Paleozoic massifs (the Bou-Mia and the Aouli). The Paleozoic substratum that crops out in these massifs consists of pelitic and quartzitic lithotypes intruded by the Hercynian granites and unconformable overlain by a Mesozoic cover consisting of Triassic evaporites/clastics and of Jurassic and Cretaceous carbonates and shales (Bouabdli et al., 2005). Located in the internal part of the Hercynian chain, the Upper Moulouya district contains one of the largest concentrations of lead in Morocco, with a total output of more than one million metric tons, and is only exceeded by the Pays des Horsts district (Rajlich, 1983). The district displays three main types of lead-barite ores: (1) Zeïda Permo-Triassic sandstone-hosted mineralization in arkosic sediments

(dates of economic ore production: 1972-1985), (2) Mibladen stratabound karstic Pb-Zn mineralization in the Liassic carbonates (1936-1985), and (3) Aouli Pb-Zn-Ag vein-type deposits hosted in the Hercynian basement (1926-1985) (Fig. 1.1) (Jébrak et al., 1998).

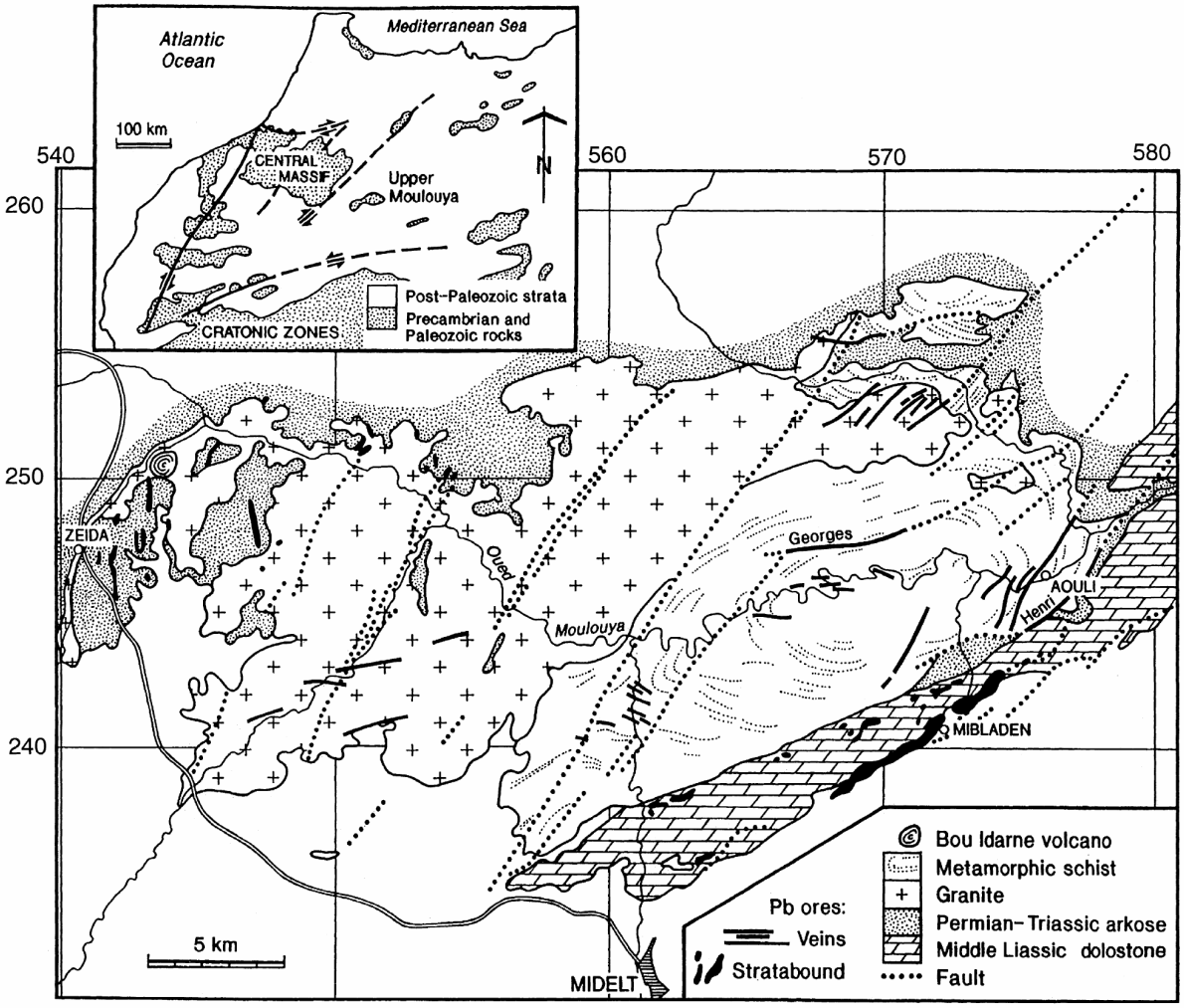

Figure 1.1. Geological map of the study area (modified from Emberger 1961).

The Zeïda mining area (1490 m asl) is located 30 km NW of the small town of Midelt over a large area along the Moulouya river's course. At Zeïda the mineralization occurs as stratabound levels in the sub-horizontal Permo-Triassic arkosic sandstones, deposited on the granite basement (Emberger, 1965b; Amade, 1965; Schmitt, 1976; Björlykke and Sangster, 1981; El Jaouani, 2001). The paragenetic association is very simple, with well crystallized

cerussite [$PbCO_3$] (70% of extracted Pb) and galena [PbS] (30%), along with minor chalcopyrite [$CuFeS_2$], pyrite [FeS_2], and large amounts of pink barite [$BaSO_4$] and scarce small yellow cubes of fluorite [CaF_2]. Barite accounts for approximately 4 wt.% of the ore. Minerals occupy interstitial voids between sand grains. The Zeïda deposit also contains noneconomic barite-galena vein lets which cross-cut the arkosic sediments and the Aouli granite. Minor anglesite [$PbSO_4$], wulfenite [$PbMoO_4$], vanadinite [$Pb_3(VO_4)Cl$], pyromorphite [$Pb(PO_4)_3Cl$] and rare sphalerite [ZnS] were also found (Amade 1965; D.M., 1990).

The Mibladen ore deposit (1400 m asl) extends over an area of about 60 km^2. The mining area is located 15 km ENE of Midelt in a plateau consisting mainly of Mesozoic carbonates covering the basement (Felenc and Lenoble, 1965). In Mibladen mainly galena and less frequently barite have been mined; but rare chalcopyrite and pyrite have been encountered as well (Petris, 1963). The most common oxidation products are cerussite, anglesite and vanadinite. Galena, often automorphic and cubic and in association with barite, occurs as impregnations, disseminations or layers of variable thickness in a shaly-dolomitic and calcareous-dolomitic sediment (Emberger, 1965a, b). The first two deposits may correspond to the same Triassic metallogenic event, focused along fault systems or within permeable sandstone. Deep fluids were mobilised during the early extensional movements associated with the opening of the Atlas rifting basin. The Mississippi Valley type Mibladen mineralization is related to a distinct metallogenic event superimposed on the earlier one, and represents a remobilization of earlier concentrations, or a more recent leaching of the same sources, but with a more pronounced contribution of the local organic matter (Jébrak et al. 1998). Galena usually appears oxidized and partially or totally replaced by cerussite and anglesite (Emberger, 1965a, b).

The Aouli mine (1130 m asl) is located 26 km NE of Midelt and at 12 km of the village of Mibladen, in a narrow gorge cut by the Moulouya river. The Aouli ore zone extends over an area of 300 km^2 and consists of a network of veins hosted by metamorphic schists and granites; minor veins also occur in the cover of Permo-Triassic sedimentary rocks (Emberger, 1965b). The main ore mineral at Aouli is galena, associated with barite and fluorite in a quartz gangue [SiO_2]; minor amounts of sphalerite, pyrite, chalcopyrite and rare malachite [$Cu_2(CO_3)(OH)_2$], azurite [$Cu_3(CO_3)_2(OH)_2$] and cerussite have been recorded (Saunier, 1963; Nasloubi, 1993).

In 1975, the Aouli and Mibladen mines were depleted and in 1985 all mines were closed. This resulted in large mining districts being abandoned with their mining and metallurgic

equipment left on the surface together with all the accompanying waste materials, including tailings. This has created an important source of contamination, progressively releasing trace elements into the environment (Saïdi, 2002; Bouabdli et al., 2005).

The mining activity has seriously modified the natural landscape of the High Moulouya. In all three mining areas, different sites are devoted to exploitation and processing activities (Fig. 1.2). Deep excavations filled with ground- and run-off water (used by the locals for irrigation and water holes for the cattle), mine adits and abandoned pits occur in the exploitation sites, where also mine wastes (tailings and coarser waste rocks) are accumulated in elongated banks up to 20 m height. Processing plants, usually built in close proximity to the villages, are characterized by the presence of several abandoned (and ruined) facilities and tailings areas. Most tailings are accumulated in dumps, preferentially located along fluvial banks without safety control. The almost general lack of vegetation cover, coupled with the typical high temperatures and strong winds of this part of Morocco, enhance the erosion and transport of waste materials. The nearby Moulouya and Mibladen Rivers, along with their tributaries, running through the area and periodically subjected to flooding, support the dispersion of contaminants (El Hachimi et al., 2006).

The current climatic conditions in the region are semi arid, with annual precipitation of 100 – 400 mm and mean annual temperatures of 12 – 14 °C. The most diffuse land use is rough grazing for cattle and sheep. Recently planted orchards, containing mainly apple trees, can be found in specific areas where the availability of water is less limited due to the occurrence of privately-owned wells.

According to the Global Soil Regions map, based on a reclassification of the FAO-UNESCO Soil Map of the World, the soils in the region of the Upper Moulouya valley are mainly entisols and inceptisols (USDA, 2005).

1.5.1 Common minerals occurring in the rock ore

The main features of the most common mineral phases occurring in the rock ore of the Upper Moulouya lead mining district are given in Table 1.1.

The most common minerals occurring in the rock ore from the High Moulouya valley are: calcite, dolomite and quartz.

The most important lead bearing minerals are anglesite, cerussite and galena.

Anglesite is a rare lead mineral and can be a beautiful specimen; it has the same structure as barite and forms very similar crystals. However, anglesite has a very high density and even though barite is a rather heavy mineral, anglesite is nearly 50% more dense. It is a secondary mineral, typically formed in the oxidation zone of galena (lead sulphide) ores.

Cerussite is a popular collection mineral, famous for its great sparkle, great density and amazing twinned crystals; the lead is responsible for its increased specific gravity. Cerussite is found in the oxidation zone of lead deposits usually associated with galena and anglesite.

Galena is a common and popular mineral for rock hounds; it is the major ore of lead and silver. The solubility of galena is very low ($K_{sp} = 10^{-28}$) and so it is inclined to precipitate.

The most important zinc bearing minerals are: hemimorphite, hydrozincite, smithsonite, sphalerite and willemite.

Hemimorphite is one of the more common sorosilicates. Its most noteworthy characteristic is its polar or *hemimorphic* crystals from where it gets its name. The crystal structure produces a different termination at each end of the crystal. One termination, the "bottom" is rather blunt being dominated by a pedion face while the opposite end, the "top" is terminated by the point of a pyramid. It is a minor ore of zinc as well as hydrozincite, which forms in the oxidation zones of zinc deposits as masses or crusts.

Smithsonite has been and is still being used as an important, although rather minor ore of zinc. Smithsonite forms in dry climates as a weathering product of primary sulphide zinc ores such as sphalerite; its features is the slight effervescence with warm hydrochloric (HCl) acid.

Sphalerite (which is also known as blende), is is by no doubt the most important ore of zinc, an industrially and at times strategically important metal. Although its importance as an ore of zinc is undisputed, it is a very attractive and a very interesting mineral for collectors as well.

Willemite is a somewhat rare zinc mineral and one of the best examples of a fluorescent mineral. Among the zinc minerals, hemimorphite and sphalerite are characterized by lower values of solubility product (respectively, 10^{-24} and 10^{-21}) and so easily inclined to precipitate.

Table 1.1. The main features of the most common mineral phases occurring in the rock ore of the Upper Moulouya lead mining district

Mineral name	Chemical formula	Solubility product (18 °C)	Class	Colour	Associated minerals	References
Anglesite	$PbSO_4$	$K_{sp} = 10^{-7.7}$	Sulphates	Usually colourless, white and yellow	Galena, cerussite, barite and limonite	Magalhaes and Silva (2003)
Barite	$BaSO_4$	$K_{sp} = 10^{-10.0}$	Sulphates	Variable but commonly colourless or white	Numerous (calcite, sulphur, vanadinite, cerussite)	Hogfeldt (1982)
Calcite	$CaCO_3$	$K_{sp} = 10^{-9.0}$	Carbonates	Variable but generally white or colourless	Numerous	Patnaik and Pradyot (2003)
Cerussite	$PbCO_3$	$K_{sp} = 10^{-13.0}$	Carbonates	Usually colourless or white	Barite, calcite, anglesite	Swanson and Fuyat (1953)
Dolomite	$CaMg(CO_3)_2$	$K_{sp} = 10^{-17.0}$	Carbonates	Often pink or pinkish	Calcite, sulphide ore minerals, barite, quartz	Howie and Broadhurst (1958); Halla (1962)
Galena	PbS	$K_{sp} = 10^{-27.5}$	Sulphides	Lead to silver gray	Calcite, dolomite, sphalerite, and other sulfide minerals	Davis et al. (1993)
Hemimorphite	$Zn_4Si_2O_7(OH)_2H_2O$	$K_{sp} = 10^{-24.0}$	Silicates	Blue-green, green, white	Limonite, aurichalcite, calcite and smithsonite	Swanson and Fuyat (1953)
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	$K_{sp} = 10^{-14.9}$	Carbonates	White or clear	Sphalerite, limonite, smithsonite, hemimorphite and calcite	Jambor and Pouliot (1965) ; Alwan and Williams (1979)
Quartz	SiO_2	-	Silicates	Variable	Numerous	Swanson and Fuyat (1953)
Smithsonite	$ZnCO_3$	$K_{sp} = 10^{-9.9}$	Carbonates	green, lavender, purple, yellow and white	Hemimorphite, cerussite, hydrozincite, calcite	Swanson and Fuyat (1953)
Sphalerite	(Zn, Fe)S	$K_{sp} = 10^{-20.6}$	Sulphides	Black	Galena, fluorite, quartz, calcite, magnetite	Vaughan and Craig (1978)
Willemite	Zn_2SiO_4	$K_{sp} = 10^{-15.7}$	Silicates	Colourless or white	Calcite, other rare minerals	Swanson and Fuyat (1953)

1.6 Aim of the study

The presence of abandoned mines along river courses has ever generated several environmental problems: mining for metals in terrestrial environments is widely recognized to increase metallic elements amounts in the soil and to impact water quality downstream from the mines (Schmiermund and Drozd, 1997). In the lead industry, Pb, Zn, Cd, Cu are released in substantial quantities (Callender, 2003).

The main purpose of this whole work was to characterize (in terms of total content and speciation) the potentially toxic metals (PTMs) contamination of mine wastes, soils, river sediments, surface and ground waters from the former lead mining district of the High Moulouya valley (Morocco) in order to correctly assess the risk/toxicity of contamination according to the mobility and transferability of the pollutants from wastes into nearby soils, stream system and vegetation.

This aim was achieved through:

- an analysis of the historical use of the site and its geological setting in relation with ore mining;
- the morphological description of mine wastes and soil profiles in the field;
- the collection of wastes, soils, sediments and waters;
- the general chemical characterization of all solid samples;
- the classification of the waters on the base of their chemical properties;
- the evaluation of PTMs total content of wastes, soils, sediments and waters;
- the measurement of the bioavailable or potentially leacheable metal fraction in wastes, soils and sediments;
- the definition of the physical and chemical partitioning of the main metallic contaminants (Pb and Zn) in selected contaminated and not contaminated wastes and soils;
- the qualitative and semi quantitative mineralogical analysis of the above selected wastes and soils.

Chapter 2 presents the waste, soil and sediment general properties (pH, EC, organic matter and total carbonates content and texture) and PTMs total and bioavailable ($CaCl_2$-extractable) content; morphological features of soil profiles are also described.

Chapter 3 works on the water properties and contamination of the Moulouya river basin: chemical characterization and PTMs total content analyses of surface water and groundwater samples collected in the study area are described in order to evaluate the impact of past mining activity on the quality of the water.

Chapter 4 focuses on the comparison between chemical (by sequential chemical extractions) and mineralogical (by XRPD) speciation defining forms and phases of Pb and Zn in wastes and soils.

Chapter 5 reports the overall conclusions.

Figure 1.2. Mining exploitation and processing areas in the Upper Moulouya district. A, B: groundwater filling deep excavation in Zeïda; C, D: waste dumps and processing plant facilities in Mibladen; E, F: ruined facilities and abandoned village in Aouli.

CHAPTER 2

GENERAL PROPERTIES AND PTMS TOTAL CONTENT OF MINE WASTES, SOILS AND RIVER SEDIMENTS

2.1 Introduction

Soil quality can be defined as the degree of sustainability to the specific functions that soils perform in a given ecosystem (Diack and Stott, 2001). There is not a single measurement that can quantify soil quality (Stewart, 1992), but there are many indicators of soil quality that can be measured including microorganism populations, basal and specific respiration rates, microbial diversity, enzyme activities (indicative approach), pH, soluble salts, cation exchange capacity, organic matter, texture, aggregate stability, water holding capacity (descriptive approach) (Diack and Stott, 2001).

Soil quality is affected by incorporation of external materials or other factors. Contaminants are considered to be soil disturbing substances, since they can generate changes in some soil properties, i.e. pH, electrical conductivity, PTMs concentration, enzymatic activity, etc. (Stamatiadis et al., 1999). Soil provides the nutrient-bearing environment that sustains plant growth. Essential nutrient metals and other metals in food crops are translocated through soil into the food web. Natural contents of potentially toxic elements in soils are generally low unless soils develop from rock with high contents of one or more elements or from ore-bearing rock. Metal contents in soils may be greatly enhanced by human activities. As an environmental geochemistry sample, soil has to be considered in terms of the soil profile which develops over time as a temporal but ever changing end product of the interactions of physical, chemical and biological processes during weathering.

The study of soils formed by human activities is one of the concerns of modern pedology (Buondonno et al., 1998). The uniqueness of the genesis, characteristics and properties of the soils in highly human-influenced environments has been pointed out by pedological investigations carried out on urban areas (Agarkova et al., 1991; Burghardt, 1994a,b), mined lands (Ciolkosz et al., 1985; Thurman and Sencindiver, 1986) and abandoned pits (Strain and Evans, 1994).

Soil properties, according to the variability in organic and inorganic soil constituents, may have a strong influence on progressive PTMs accumulation (Alloway, 1995).

An evaluation of the retention, release and distribution of PTMs in soils is a determining step in various types of geoenvironmental studies (Adamo et al., 2002). The decrease in mobility, or the retention, of PTMs and their distribution among geochemical phases of the soil depends upon compositional and state characteristics of the soil solids (mineralogy, grain size, compaction, water content, etc.) and of the pore fluid (pH, temperature) (Santillan-Medrano and Jurinak, 1975; Farrah and Pickering, 1977, 1978). The complexity of the interactions is complicated by the heterogeneous nature of the different soil constituents (Selim and Sparks, 2001). PTMs movement with water in soils, requires their presence in a soluble state or an association with mobile particulates. Particulates could complex metals in the topsoil and carry them downward the profile where they would be in an exchangeable form. Movement of metals in soil is strongly related to the particular physical-chemical form of the element. Soil redox status strongly affects element forms and mobility and, generally, PTMs are less soluble in their higher oxidation states (Sposito, 1984; McBride, 1989).

Critical phases in planning a study to assess the health status of an ecosystem are: 1) determining which samples can be used; 2) understanding what the sample represent in space and time; 3) knowing how chemical elements may be bound in a sample, physically and chemically; 4) establishing an ideal scale of sampling with realistic modifications as a function of where a sample type can be collected. There are several factors that must be determined in an area before selecting a remediation methodology that is considered to be best suited for cleanup of PTMs contaminated soils and then initiating a pilot study. These include the extent and thickness of the polluted soils, soil texture (sand, silt, clay contents), porosity and permeability, organic matter content, mineralogy, chemical composition and how target metals are bound in the soil (extractability).

In a preliminary phase of pollution assessment, it can be also useful to rationalize the information obtained by acid digestion for total concentration. This can be done by comparing the concentrations in different solid samples as representatives of various areas of a site: natural soils as background samples, tailings from mining and milling activities, stream or lake sediments. These comparisons can reveal mobilization phenomena from source points, but also from one kind of solid matrix to others (e.g. from metal-bearing tailings to the surrounding soil). Further information can also be obtained by relating total concentrations to soil texture (Giuliano et al., 2007). It is quite generally observed that size fractions with lower dimensions present larger pollutant concentrations according to their higher specific area (grain size effect). Consequently, significant correlations between particle size distribution of

soil samples and total concentrations can show how surface interactions, associated with anthropogenic contributions, predominate (Adamo et al., 1996; Huang and Lin, 2003).

Physical fractionation is based on the concept that the association of SOM with particles of different size and different mineralogical composition differ in structure and function (Christensen, 1992). Heavy metals associated with particles of different size can therefore differ in their stability and accessibility, e.g. clay-sized particles provide a large surface area and numerous reactive sites where SOM and metals can be sorbed by strong ligand exchange and polyvalent cation bridges (Sposito et al., 1999), thus determining a greater stability. The distribution of heavy metals in different soil fractions can therefore mirrors differences in metal availability and environmental impact.

Maximum contaminant levels (MCLs) for PTMs and other inorganic and organic components in water and foods have been set by various organizations. These entities include the World Health Organization (WHO), the Pan American Health Organization (PAHO), the Environmental Protection Agency (EPA) in the United States, and the European Health Union (EHU). The MCLs have been determined from careful and ongoing laboratory investigations and from medical records and observations on ingestion of PTMs, their bioaccumulation factors and their impact on human health. The MCLs published by one organization do not always agree with those from others but are of the same order of magnitude and close in value. Data from global and national organizations for allowable concentrations of PTMs in soils are not as complete or as uniform as for drinking water. When a metal has concentrations that exceed its MCL in published values for others media considered critical to human health status, alerted public health authorities work to put remediation action plans into operation (Siegel, 2002).

The main objective of this work was to characterize physically and chemically the wastes, soils and river sediments taken from the Zeïda, Mibladen and Aouli mining areas in order to assess the main pollutants, their level of contamination, their distribution with depth and among different particle size fractions and their mobility/bioavailability as assessed by 0.1M $CaCl_2$ extraction.

2.2 Material and methods

2.2.1 Sample collection

Mine waste, soil and river sediment sampling was carried out in three campaigns: February 2007, November 2007 and April 2008.

The sampling network was designed collecting surface soil, river sediment and mine waste samples in several points (26) in and outside the mining areas and along the Moulouya river stream; a total of 41 samples (approximately 1 kg each) were collected at various depth using a stainless steel trowel and subsequently transferred to clean polypropylene bags. Sample points were located by Global Position System (GPS).

In Fig. 2.1 and Table 2.1, the location of the sampling sites are given.

In particular, within the mine areas, particles were sorted into different sizes during the construction process: close to the dumping site coarse grained materials were deposited (coarse waste rock), while far from it only fine grained materials and precipitates were accumulated (tailings).

Waste samples were collected from the mine waste dumps inside the exploitation and the processing sites of the three mines.

River sediment samples were collected in correspondence of the processing sites of Zeïda and Aouli.

Potentially unaffected surface soil samples and river sediments were also taken randomly at various locations outside the mining areas.

As regard soil, six profiles were opened, described and sampled from each horizon at selected locations inside the exploitation and processing sites of Zeïda and Mibladen areas and outside Zeïda mine area.

Table 2.1. Location of studied mine wastes, soils and river sediments

N°	Sample code	Site	Latitude	Longitude
			N	W
	Mine Z (Zeïda)			
1	ZP1	Expl.	32° 48' 26"	4° 58' 17"
2	ZC	Expl.	32° 48' 10"	4° 58' 32"
3	ZP2	Proc.	32° 50' 19"	4° 57' 20"
4	ZT	Proc.	32° 50' 24"	4° 57' 05"
5	ZS	Proc.	32° 50' 29"	4° 57' 08"
6	Zsed	Proc.	32° 50' 19"	4° 57' 20"
7	ZP3	out	32° 47' 27"	4° 57' 51"
8	SS1	out	32° 50' 45"	4° 54' 02"
9	SS2	out	32° 45' 30"	4° 59' 32"
	Mine M (Mibladen)			
10	MP1	Expl.	32° 45' 16"	4° 39' 02"
11	MC2	Expl.	32° 45' 15"	4° 39' 10"
12	MP2	Proc.	32° 45' 42"	4° 38' 41"
13	MP3	Proc.	32° 45' 53"	4° 38' 41"
14	MT	Proc.	32° 45' 44"	4° 38' 40"
15	MC1	Proc.	32° 45' 39"	4° 38' 43"
16	SS	out	32° 40' 57"	4° 37' 27"
17	SS3	out	32° 38' 47"	4° 46' 24"
18	SS4	out	32° 41' 56"	4° 42' 58"
19	SS5	out	32° 43' 52"	4° 40' 57"
20	SS6	out	32° 43' 29"	4° 40' 33"
21	SS7	out	32° 43' 54"	4° 43' 22"
22	SS8	out	32° 45' 37"	4° 47' 36"
23	sed	out	32° 41' 56"	4° 41' 55"
	Mine A (Aouli)			
24	AT	Proc.	32° 48' 40"	4° 35' 34"
25	Ased	Proc.	32° 48' 27"	4° 36' 02"
26	AC	Proc.	32° 49' 23"	4° 34' 40"

P = soil profile; C = coarse waste rock; T = tailing; S = surface soil; sed= river sediment; Expl. = exploitation area; Proc.: processing area; out = outside mining area

2.2.2 Analytical procedures

Soil profiles were described soon after opening and the following main properties were determined in the field:

- Horizons boundaries: the change from one horizon to another varies in distinctness (abrupt < 2 cm; clear 5 – 10 cm) and outline (smooth = almost straight; wavy = gently undulating) and is usually caused by differences in colour.
- Texture: soil particles are divided initially into two size classes with the limit set at 2 mm to delimit the "fine earth" from the skeleton (>2 mm).
- Colour: a very high proportion of the names of soils is based upon colour, since this is the most conspicuous property and sometimes the only one that is easily remembered. Generally the colour of a soil is determined by the amount and state of iron and/or organic matter. The colour was determined on samples using the Munsell Soil Colour Charts (Munsell Color, 2000); this semi-quantitative method of colour measurement depends on visual matching of a soil sample with standard colour chips.
- Structure: this refers to the degree and type of aggregation; in many soils the individual particles exists as discrete entities but in others the most common arrangement is for the particles to be grouped into aggregates with fairly distinctive shapes and sizes. The main types of structures found were: platy (the units are flat and platelike, generally oriented horizontally), blocky (the structural units are blocklike or polyhedral), granular (the structural units are approximately spherical), massive (structureless).
- Carbonate content: based on sample effervescence observed after adding HCl 10% (Siebe et al., 1996).

The characterization of all samples was carried out at the Department of Soil, Plant, Environmental and Animal Production Science of the University Federico II of Napoli (Italy). Solid samples were preliminary characterised to relate their properties to the total concentration of toxic elements obtained by acid digestion.

Once in the laboratory, all bulk samples were air dried at room temperature and sieved at 2 mm, obtaining the soil skeleton (the >2 mm fraction) and the fine earth (the <2 mm fraction). Particle-size analysis was carried out after low-energy ultrasonic treatment at 20 kHz and 75 W for 15 min with the Andreasen's pipette method. Particle-size fractionation (2 mm – 10 µm; 10 µm – 2 µm; <2 µm) was carried out on selected samples by centrifugation.

On the fine earth fraction the following analyses were carried out:

- moisture content at 105 °C;
- pH (H_2O) (1:2.5, soil:water ratio);
- pH ($CaCl_2$) (1:2.5, soil:0.01M solution ratio);
- electrical conductivity (EC) (1:5, soil:water extract at 25 °C);
- organic carbon content (OC) based on rapid dichromate oxidation (Walkley and Black method, 1934);
- inorganic carbon (carbonates) content by pressure Dietrich–Fruehling calcimeter method (Loeppert and Suarez, 1996);
- Al, Si and Fe forms by oxalate (Schwertmann, 1964) and dithionite-citrate (Holmgren, 1967) extractions.
- multielement (Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hf, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Sn, Sr, Ta, Th, Ti, U, V, W, Y, Zn, Zr) analysis by acid digestion (18:10:3:6 H_2O-HF-$HClO_4$-HNO_3) on hot plate with recover of the residue by dissolution in dilute (15%) aqua regia of 2:2:2 HCl-HNO_3-H_2O (ACS grade) heated in a boiling water (> 95 °C) bath for 30 minutes. Sample solutions were analyzed by a Perkin Elmer Elan 6000 ICP mass spectrometer. This analysis was carried out at ACME Analytical Laboratories LTD., Vancouver, Canada, through Norwest Italia s.r.l.;
- potentially toxic metal bioavailability by single extraction in 0.01M $CaCl_2$ (Novozamsky et al., 1993).

2.2.3 Statistical analysis

Simple correlation analyses were carried out for all obtained data using the commercially available software package STATISTICA™. The evaluation of the degree of association among variables was based on calculating the value of the Spearman's rank correlation coefficient (r) and testing it for 5% significance level.

2.3 Results and discussion

2.3.1 Soil profiles morphological features

The morphological features of the soil profiles are in Figures 2.2 and 2.3 and in Table 2.2.

Zeïda mining area

In the area of Zeïda mine, three soil profiles were opened: ZP1, ZP2 and ZP3.

ZP1 was opened in the exploitation area of Zeïda. The section (Fig. 2.2A), opened until 52 cm of depth, was described with the following horizons: Ck (0–6 cm), 2Ck (6–36 cm), 3Ck (36–52 cm). The surface horizon was characterized by red colour, blocky structure and occurrence of few organic matter and roots; it appeared quite different from the others and the abrupt boundary suggested for it an anthropic origin. All horizons were characterized by a high content of skeleton (30-40%) and by a strong effervescence in HCl indication of carbonates occurrence.

ZP2 was opened in the processing or industrial area of Zeïda, between the Moulouya river and a smaller torrent, close to the site where tailings were commonly discharged and stored. This area, uncultivated at the sampling time, showed signs of a former agricultural use. Periodic overflows of the streams contributed to add coarse grained materials to the area and contemporarily to carry away tailings. In ZP2 from the surface to 60 cm of depth, the following horizons were found: Ak (0–10 cm), 2Bk1 (10–27 cm), 3Bk2 (27–60 cm) (Fig. 2.2B). Different colours and clear boundaries evidenced the natural origin of this profile. All horizons showed a blocky structure and a lack of organic matter and roots. The skeleton was found only in the first two horizons. Also in ZP2 effervescence in HCl was strong indicating consistent occurrence of carbonates.

ZP3 was opened outside the proper Zeïda mining area in a field cultivated with potatoes in the proximity of Zeïda city. The section (Fig. 2.2C), opened until 70 cm of depth, was described with the following horizons: Ak (0–9 cm), 2Bk1 (9–25 cm), 3Bk2 (25–40 cm), Ck(40–70 cm). Colour, structure and clear boundaries evidenced that main soil forming factors were natural. The first two horizons were characterized by a blocky structure, common occurrence of organic matter and roots and low content of skeleton (10%). The deepest horizon showed light brown colour, massive structure and lack of organic matter and skeleton. Effervescence by HCl in this profile was less pronounced compared with ZP1 and ZP2.

Table 2.2. Morphological features of the soil profiles

Soil profile	Horizon	Depth *(cm)*	Limits	Main soil forming factor	Colour [dry]	Structure	Skeleton	O.M. and roots	Mottling	HCl effervescence
Zeïda										
ZP1	Ck	0-6	abrupt smooth	Anthropic	2.5 YR 4/6 (red)	blocky	40%	few	none	strongly
	2Ck	6-36	clear smooth	Natural	7.5 YR 4/6 (strong brown)	blocky	40%	few	none	strongly
	3Ck	36-52		Natural	7.5 YR 4/6 (strong brown)	massive	30%	absent	none	strongly
ZP2	Ak	0-10	clear smooth	Natural	5 YR 6/8 (reddish yellow)	blocky	10%	few	none	strongly
	2Bk1	10-27	clear wavy	Natural	7.5 YR 5/6 (strong brown)	blocky	20%	absent	none	strongly
	3Bk2	27-60		Natural	5 YR 7/4 (pink)	blocky	absent	absent	none	strongly
ZP3	Ak	0-9	clear wavy	Natural	5 YR 5/6 (yellowish red)	blocky	10%	common	none	slightly
	2Bk1	9-25	clear smooth	Natural	7.5 YR 5/6 (strong brown)	blocky	10%	common	none	slightly
	3Bk2	25-40	abrupt smooth	Natural	7.5 YR 6/4 (light brown)	blocky	absent	few	none	slightly
	Ck	40-70		Natural	7.5 YR 6/4 (light brown)	massive	absent	absent	none	slightly
Mibladen										
MP1	Ak	0-15	abrupt smooth	Anthropic	5 YR 5/6 (yellowish red)	granular	absent	many	few	slightly
	2Bk	15-45	abrupt smooth	Anthropic	5 YR 4/6 (yellowish red)	granular	absent	many	few	slightly
	3Ckm	45-75		Natural	7.5 YR 5/6 (strong brown)	massive	absent	few	none	slightly
MP2	Ck	0-23	abrupt smooth	Anthropic	7.5 YR 6/4 (light brown)	granular	absent	few	clear	strongly
	2Ck	23-50	abrupt smooth	Anthropic	7.5 YR 7/4 (pink)	granular	70%	absent	none	strongly
	3Ckm	50-90		Anthropic	2.5 YR 4/6 (red)	massive	40%	absent	clear	strongly
MP3	Ck	0-35	abrupt smooth	Anthropic	7.5 YR 6/4 (light brown)	platy	absent	few	few	slightly
	2Abk	35-45	clear wavy	Anthropic	5 YR 7/4 (pink)	granular	absent	common	none	slightly
	3Ck	45-72	abrupt smooth	Anthropic	7.5 YR 8/3 (pink)	platy	absent	absent	few	slightly
	4Ck	72-92	abrupt smooth	Anthropic	7.5 YR 7/3 (pink)	platy	absent	common	none	slightly
	5Ck	92-150		Anthropic	7.5 YR 8/3 (pink)	platy	absent	absent	clear	slightly

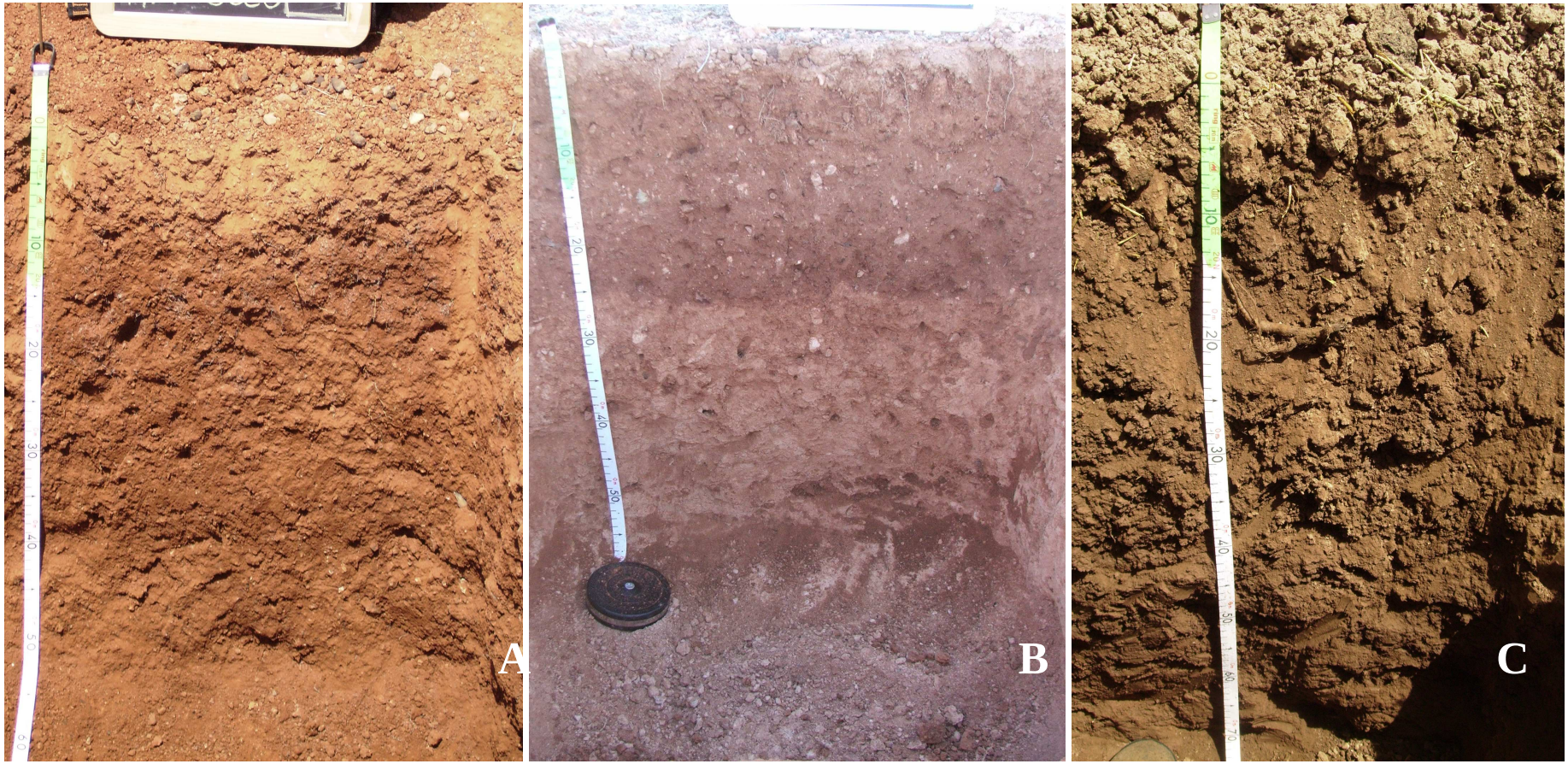

Figure 2.2. Soil profiles opened in the Zeïda mining area; A: ZP1, B: ZP2, C: ZP3.

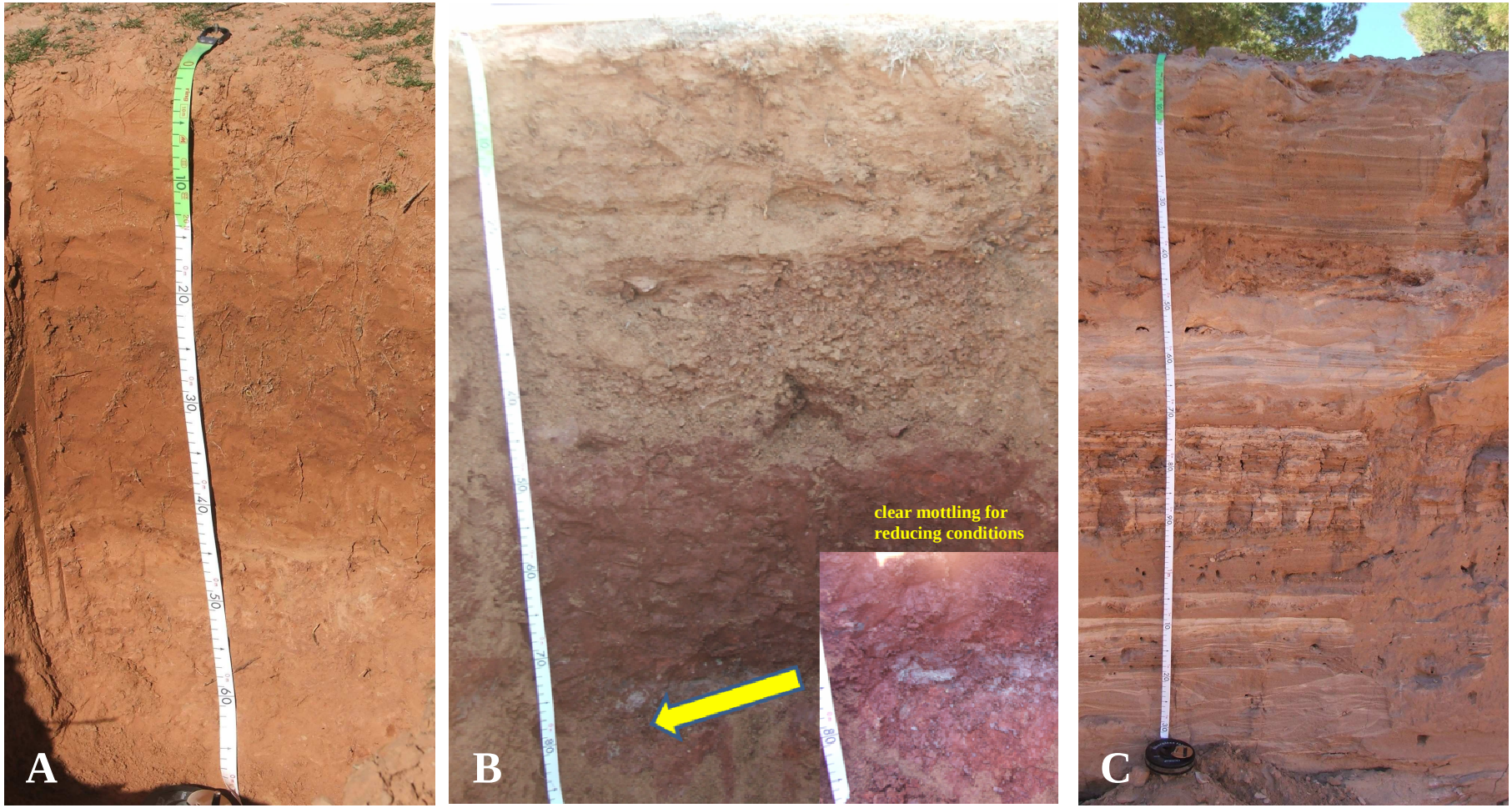

Figure 2.3. Soil profiles opened in the Mibladen mining area; A: MP1, B: MP2, C: MP3.

Mibladen mining area

In the area of Mibladen mine three soil profiles were opened: MP1, MP2 and MP3.

MP1 profile (Fig. 2.3A) was opened just outside the exploitation area of Mibladen. From the surface to 75 cm of depth, the following horizons were found, separated by abroupt boundaries: Ak (0–15 cm), 2Bk (15–45 cm), 3Ckm (45–75 cm). All horizons were characterized by a lack of skeleton and a slight effervescence by HCl. Granular structure was found in the first two horizons (Ak and 2Bk) which, although anthropic in origin on the base of colour, were enriched in organic matter and roots. The deepest horizon (3Ckm) was completely different from the above ones and characterized by massive structure and a lack of organic matter; its strong brown colour attested its natural origin.

MP2 and MP3 were both opened inside the processing or industrial area of Mibladen. They were both extremely complex as a consequence of the heavy impact of human activities on the site. All their layers did not show any significant evidence of pedogenesis and exhibited high variability in colour, structure, compactness, grain-size and mottling pointing out the extensive variability of sediment heterogeneity in the area.

MP2 was opened besides one big dumping site where coarse grained materials were used to be deposited. The site was characterized by lack of vegetation, mainly made by shrubs and grasses, and by outcropping rocks. The section (Fig. 2.3B) was opened until 90 cm of depth and characterized by the following horizons: Ck (0–23 cm), 2Ck (23–50 cm), 3Ckm (50–90 cm). The stratification and abrupt linear limits between horizons suggested a strong anthropic influence on soil formation. The skeleton was absent in the surface horizon, while it largely occurred as sub-rounded and sub-angular in the deeper horizons (respectively, 70% and 40%). Ck and 2Ck horizons were characterized by fine granular structure and low amount of organic matter and roots. The deepest horizon (3Ckm) was characterized by a massive structure; clear mottling with typical and strong grey-greenish colour was observed at 80 cm of depth, indicating reducing conditions due to drainage occlusion. All horizons were characterized by high content of carbonates as showed by HCl effervescence.

MP3 section (Fig. 2.3C) was opened along the bank of a torrent (dried during the sampling) at the bottom slopes of a big tailings dump. Sampling site was characterized by the occurrence of numerous trees (conifer) and several grass herbaceous species. The section, opened until 150 cm of depth, was described with the following horizons: Ck (0–35 cm), 2Abk (35–45 cm), 3Ck (45–72 cm), 4Ck (72–92 cm), 5Ck (92–150 cm). All C horizons, characterized by a lack of pedogenesis evidences and by microlaminations and platy structure, appeared mainly made by materials of similar morphology and organized in series of overlying thin layers.

Probably, the transport of sediments and sludge by surface waters contributed to the horizons formation. 2Abk horizon had a different colour and lack of laminations and a slight granular structure. All horizons were enriched in carbonates. The occurrence of organic matter (leaves, pine needles and wooden twigs), roots and, in the surface horizon, clear evidences of biological life induced to hypnotise that the area was periodically colonized by vegetation, whose stabilization was disturbed by new sludge and river sediments arrivals (i.e. colluvial and alluvial processes). The deepest horizon (5Ck) was characterized by the presence of very clear mottling. All horizons were characterized by a high content of carbonates.

2.3.2 Main physical and chemical properties of wastes, soils and sediments

The main chemical properties of mine wastes, soils and river sediments are presented in Table 2.3.

As expected, the percentage of fine earth was low in all coarse waste rock samples (ZC: 76%; MC1: 28%; MC2: 58%; AC: 8%), while no particles larger than 2 mm were found in the tailings, which were crushed during the ore extraction process. Soil samples from the exploitation and processing sites were characterized by variable amounts of particles larger than 2 mm, according to the variable contribution of coarse and fine wastes to soil formation. The content of particles larger than 2 mm was particularly high in the sub-surface horizons of MP2 and in all horizons of ZP1; both soil profiles were opened besides coarse waste dumps. On the contrary, particles with diameter > 2 mm were not found in all horizons of MP3 which was opened in the proximity of a big tailings dump. Sediments were mostly made by fine earth particles.

The pH ($CaCl_2$) of all samples ranged from 7.5 to 8.5 presumably as a consequence of $CaCO_3$ abundance due to limestone environment. The pH (H_2O) was also sub-alkaline or alkaline but more variable and ranging from 7.9 to 9.4. Higher values seem to characterize the waste materials compared to soil and sediment materials. EC ranges from 0.1 in ZT to 2.1-2.2 in MP1. The salt content of the soil solution strongly influences the pH of the soil. As confirmed by the Spearman correlation coefficient, the difference between pH (H_2O) and pH ($CaCl_2$) was strictly correlated with the EC values: such difference decreases with EC increasing, indicating that the high content of salt lower the pH (H_2O) values (r: - 0.859; p-level < 0.001). The highest content of $CaCO_3$ was found is soils (average: 485 g kg^{-1}) and mine wastes (558 g kg^{-1}) from the Mibladen processing area; the lowest content of $CaCO_3$ occurred in Zeïda mine wastes (ZC: 72 g kg^{-1} and ZT: 2 g kg^{-1}), because of the granite-sandstone host of the mineralization, and in Aouli coarse waste rock (AC: 93 g kg^{-1}). The majority of studied

samples had no or very low content of organic matter, which in only a few cases was higher than 10 g kg^{-1} and reached a maximum value of 36 g kg^{-1} (SS3). In general, the content of organic matter of soils outside the mining areas was always higher than that of samples taken from inside the mining areas (average values of 16 g kg^{-1} > 6 g kg^{-1}, respectively).

The dissolution data in Table 2.4 may be considered as indicators of crystalline and poorly crystalline iron oxides (Buondonno and Coppola, 2005), which frequently represent a significant part of the colloidal fractions of soils and sediments and which, according with their high specific surface area, disordered network and high charge density react readily with anions, cations and organic molecules. According to these data, the Fe_o/Fe_d ratio for the analysed materials indicated the dominance of crystalline iron oxides.

2.3.3 Multielement analysis of wastes, soils and sediments

The total content of alkaline and alkaline earth metals (Li, Na, K, Rb, Be, Mg, Ca, Sr, Ba), transition metals (Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd), lantanides (La, Ce), attinides (Th, U), metals (Al, Sn, Pb) and metalloids (As, Sb, Bi) in all samples collected in Zeïda, Mibladen and Aouli mining areas are reported in Tables 2.5, 2.6 and 2.7.

The total content of all elements in wastes, soils and sediments was measured both on skeleton (fraction A: particles diameter > 2 mm) and fine earth (fraction B: particles diameter < 2 mm). The total element content of the whole sample was obtained by summing the values determined in the two grain size fractions after multiplying the mg of metal kg^{-1} of fraction A or B for the percentages of A and B fraction in soil.

Taking into account the lack in literature of ‘consolidated background values’ for the studied geographical area, the PTMs concentration limits imposed by the Italian Ministry of Environment (DM 152/06) for soils (Table 2.8), were used as possible reference for a preliminary ‘contamination’ evaluation.

In agreement with other results from the literature, the main metallic contaminants in the studied area are Pb and Zn which in several samples are associated to high values of Cu, Co, As, Cd, Sb, V and Sn (Fig. 2.4 – 2.6).

Samples from the Zeïda exploitation area did not show any evidence of severe contamination: both mine waste (ZC) and soil profile (ZP1) were characterized by Pb and As contents slightly higher than the limits (Pb: 100 mg kg^{-1}; As: 20 mg kg^{-1}) imposed for soils of public, residential and private areas.

In the processing area of Zeïda the majority of the samples (ZT, ZP2 and ZS) were contaminated: in particular, the mine tailings were highly enriched in Pb (4131 mg kg^{-1}) and Zn (568 mg kg^{-1}).

In all soil samples (ZP3, SS1 and SS2) taken from outside the exploitation and processing areas of Zeïda, none PTMs content was above maximum concentrations.

In the Mibladen area all mine wastes (MC1, MC2 and MT) were highly enriched in Pb and Zn. Strong contamination of the soil profiles was found in the processing area of Mibladen. MP2 showed in the surface horizon the highest value of Zn (189342 mg kg^{-1}) and very high contents of Cu (average: 249 mg kg^{-1}), Pb (11875 mg kg^{-1}), As (162 mg kg^{-1}) and Cd (602 mg kg^{-1}). MP3 had very high content of Pb and, only in the surface horizon, also high values of Cu (348 mg kg^{-1}), Zn (3083 mg kg^{-1}), Cd (16 mg kg^{-1}) and Sb (11 mg kg^{-1}).

As observed in Zeïda, the soil profile opened in the Mibladen exploitation area (MP1) as well as surface soils and river sediment sampled outside Mibladen area were essentially uncontaminated; only SS sample had Zn (174 mg kg^{-1}), Co (24 mg kg^{-1}), As (19 mg kg^{-1}), V (421 mg kg^{-1}) and Cr (149 mg kg^{-1}) contents slightly exceeding regulatory levels.

Wastes from Aouli mining area (AC and AT) were also enriched in Pb and Zn; in the coarse waste rock sample (AC) also Cu total content was above maximum concentration.

The analysis of correlation revealed, as shown in Fig. 2.7, statistically significant direct relationship between the content of Pb, Sb, Ag and Cu ($r = 0.885$; $r = 0.911$; $r = 0.757$, respectively) and between Sb, Ag and Cu ($r = 0.916$; $r = 0.787$, respectively). Because of the geology of the Upper Moulouya mining district, the occurrence of these metal associations was expected. As reported in Chapter 1, galena was the main mined ore mineral and galena deposits usually contain significant amounts of silver as included silver sulfide mineral phases or as limited solid solution within the galena structure; in addition, zinc, antimony, cadmium, copper and arsenic also occur in variable amounts in lead ores. Antimony is geochemically categorized as a chalcophile element, occurring with sulphur and the metals lead, copper and silver.

The vertical distribution of metal contaminants in soils is given in Figures 2.8 and 2.9.

Along ZP1 soil profile, As showed a slight decreasing trend with depth although its values in the deeper horizons were still above regulatory limits (in Table 2.8). The values of Pb were above regulatory limits in all horizons and strictly correlated ($p < 0.001$) with those of Zn ($r = 0.977$) and Cd ($r = 0.846$).

In ZP2 Pb was found in high content till 30 cm depth, while it was almost absent below 30 cm; Cu, Zn and Cd were characterized by a similar behaviour with a slight decreasing trend with depth and values always lower than regulatory limits (in Table 2.8).

In ZP3 all metal contaminants were at all depths below the regulatory limits; nevertheless the major contaminants, Pb and Zn, occurred in the surface horizons in higher amounts than in the subsurface horizons, suggesting a contribution to metal loads of particles transferred by wind.

In Mibladen, MP1 was essentially uncontaminated and all metals showed a similar behaviour: in particular, the content of Pb was strictly correlated ($p < 0.001$) with those of Cu ($r = 0.933$) and Zn ($r = 0.825$).

The most contaminated MP2 soil profile had a very high content of Zn in the surface horizon which decreased with depth although it remained above regulatory levels even in the deepest horizon; Cu and Pb also showed a decreasing trend with depth and their content was strictly correlated ($r = 0.938$; $p < 0.001$). Cd and As had an uneven behaviour showing their lowest values in the sub-surface horizon (23-50 cm) and their contents were also highly correlated ($r = 0.999$; $p < 0.001$).

In MP3, Cu, Zn and Cd were very high and above regulatory levels till 35 cm depth and almost absent in the following horizons; Pb and As showed values strongly changing from one to another horizon: horizons 2Abk (35-45 cm) and 4Ck (72–92 cm) were the most highly contaminated ones (respectively, Pb: 14264 and 17205 mg kg^{-1}; As: 19 and 23 mg kg^{-1}), while the surface horizon (Ck, 0-35 cm), the horizon in between (3Ck, 45-72 cm) and the deepest one (5Ck, 92-150 cm) were all less contaminated.

According with data given in Table 2.3 relative to the percentage of the fine earth in collected samples, for all elements the contribution of the particles with diameter > 2 mm (skeleton fraction) to the total metal content (Tables 2.5, 2.6, 2.7) was relevant in all coarse waste rock samples (ZC: 24%; MC1: 72%, MC2: 42%; AC: 92%) and in soil profile from the exploitation area of Zeïda (ZP1: 36%). In all tailings, river sediments and soil profiles MP1 and MP3, particles greater than 2 mm were absent and so the total metal content was exclusively made up by the fine earth fraction. In all other samples the majority of the element total content originated from the fine earth fraction.

Table 2.3. Main chemical properties of mine wastes, soil and river sediments from the Moulouya river valley

Sample code	Depth *[cm]*	Fine earth *[%]*	pH ($CaCl_2$)	pH (H_2O)	EC *[dS m^{-1}]*	O.M. *[g kg^{-1}]*	Carbonates *[g kg^{-1}]*
Mine Z (Zeïda)							
ZC	0-20	76	8.0	8.3	1.2	4.0	72
ZT	0-20	100	7.9	9.2	0.1	3.0	2
ZP1	0-6	63	8.3	8.9	1.7	absent	204
	6-36	62	8.1	8.8	1.6	absent	259
	36-52	66	8.1	8.5	1.9	absent	266
ZP2	0-10	75	8.1	9.2	0.2	13.0	427
	10-27	79	8.1	8.8	0.3	11.0	400
	27-60	89	8.1	8.8	0.3	9.0	696
ZP3	0-9	88	8.0	8.7	0.8	28.0	276
	9-25	81	8.0	8.6	0.6	24.0	274
	25-40	94	8.0	8.6	0.5	20.0	280
	40-70	100	8.1	8.8	0.9	16.0	236
ZS	0-10	100	7.9	8.1	1.8	27.0	244
SS1	0-10	59	7.9	8.4	0.9	12.0	144
SS2	0-20	96	7.9	8.6	0.9	20.0	150
Zsed	0-10	100	7.8	8.6	0.2	10.0	263
Mine M (Mibladen)							
MC1	0-20	28	8.2	9.4	0.1	2.0	603
MC2	0-20	58	8.1	8.5	0.3	6.0	437
MT	0-20	100	8.0	9.1	0.1	1.0	513
MP1	0-15	100	7.7	7.9	2.2	9.0	231
	15-45	100	7.9	8.0	2.1	12.0	209
	45-75	100	7.9	8.1	2.2	7.0	154
MP2	0-23	92	7.6	8.3	0.3	6.0	452
	23-50	34	7.8	8.6	0.1	4.0	500
	50-90	32	7.9	8.8	0.2	absent	350
MP3	0-35	100	8.5	9.3	0.2	4.0	470
	35-45	98	8.4	9.2	0.1	6.0	514
	45-72	100	8.1	9.2	0.2	4.0	540
	72-92	100	8.4	8.6	1.8	8.0	456
	92-150	100	8.5	8.9	0.8	5.0	604

Table 2.3 (continued). Main chemical properties of mine wastes, soil and river sediments from the Moulouya river valley

Sample code	Depth *[cm]*	Fine earth *[%]*	pH ($CaCl_2$)	pH (H_2O)	EC *[dS m^{-1}]*	O.M. *[g kg^{-1}]*	Carbonates *[g kg^{-1}]*
Mine M (Mibladen)							
SS	0-10	100	8.0	8.8	1.3	5.0	211
SS3	0-10	100	7.5	8.1	0.5	36.0	441
SS4	0-10	100	7.8	8.3	0.2	9.0	367
SS5	0-10	90	8.0	8.6	0.5	10.0	158
SS6	0-10	84	7.8	8.7	0.3	14.0	287
SS7	0-15	99	8.0	8.4	0.7	11.0	151
SS8	0-5	82	7.7	8.3	0.5	9.0	155
sed	0-5	84	7.6	8.1	0.6	8.0	354
Mine A (Aouli)							
AC	0-20	8	7.9	8.5	0.1	3.0	93
AT	0-20	100	8.1	8.4	1.3	5.0	337
Ased	0-20	100	7.9	8.8	0.2	5.0	350

Table 2.4. Fe content (mg kg^{-1}) extractable in ammonium-oxalate and dithionite (Fe_o, Fe_d) of selected soils, river sediments and wastes from the mining areas of the Moulouya valley. Fe_{est} = estimated ferrihydrite content

Sample code	Depth (cm)	Fe_o (mg kg^{-1})	Fe_d (mg kg^{-1})	Fe_o/Fe_d	Fe_{est} (mg kg^{-1})
ZT	0-20	1.42	3.11	0.455	2.41
ZP1	0-6	1.15	17.05	0.068	1.96
	6-36	1.37	18.48	0.074	2.32
	36-52	1.70	22.81	0.074	2.88
ZP2	0-10	0.65	14.41	0.045	1.11
	10-27	0.55	14.36	0.039	0.94
	27-60	0.23	8.27	0.028	0.39
ZP3	0-9	1.87	19.60	0.095	3.17
	9-25	2.01	18.35	0.110	3.42
	25-40	1.26	19.70	0.064	2.14
	40-70	2.33	22.25	0.105	3.97
ZS	0-10	1.10	12.95	0.085	1.87
Zsed	0-10	1.02	21.79	0.047	1.74
MC1	0-20	1.09	8.11	0.134	1.85
MT	0-20	0.91	5.85	0.156	1.55
MP1	0-15	0.70	9.87	0.071	1.19
	15-45	1.13	11.11	0.101	1.91
	45-75	1.01	10.22	0.099	1.72
MP2	0-23	1.23	10.65	0.115	2.08
	50-90	1.55	12.05	0.128	2.63
MP3	0-35	1.40	10.45	0.134	2.38
	35-45	2.19	11.46	0.191	3.73
	45-72	1.86	4.85	0.383	3.16
	72-92	4.08	20.21	0.202	6.93
	92-150	1.87	7.20	0.260	3.18
SS	0-10	1.76	30.13	0.059	3.00
SS6	0-10	0.82	10.37	0.080	1.40
AT	0-20	1.20	11.04	0.109	2.04
Ased	0-20	1.72	14.73		2.92

Table 2.5. Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Zeïda mining area and total amounts (A + B)

Sample code	Depth	Fraction	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Sc
	cm		*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
ZC	0-20	A	50.2	1.13	15.2	79.0	8	14.8	80.7	322	927	8
		B	56.1	1.27	15.2	79.2	7	15.9	29.5	357	1474	9
		Tot	54.7	1.24	15.2	79.1	7	15.7	41.9	349	1341	9
ZT	0-20	B	64.8	6.36	45.2	167.1	4	1.5	12.4	1128	2746	2
ZP1	0-6	A	25.8	0.86	9.5	58.1	2	8.6	260.6	562	632	5
		B	61.8	1.60	22.3	111.6	4	10.6	99.4	291	1234	7
		Tot	48.4	1.32	17.5	91.6	3	9.8	159.4	392	1010	6
	6-36	A	35.3	1.13	14.0	83.0	3	10.6	217.0	576	946	6
		B	50.2	1.55	21.3	122.2	3	10.3	99.4	410	990	7
		Tot	44.6	1.39	18.5	107.3	3	10.4	143.9	473	973	7
	36-52	A	44.3	1.30	15.7	109.8	5	12.1	190.0	640	1442	6
		B	61.8	1.60	21.0	152.5	6	14.1	109.1	591	762	8
		Tot	55.8	1.50	19.2	137.8	6	13.4	136.8	608	995	7
ZP2	0-10	A	17.8	0.52	7.0	29.9	<1	6.1	235.7	217	1126	3
		B	27.9	1.52	11.5	46.9	1	8.6	154.5	259	2965	5
		Tot	25.4	1.27	10.4	42.7	1	7.9	174.5	249	2511	5
	10-27	A	18.5	0.71	7.9	34.8	<1	7.3	237.7	223	1136	4
		B	28.7	1.69	11.7	50.0	1	9.8	146.0	269	3316	6
		Tot	26.5	1.48	10.9	46.8	1	9.2	165.5	260	2852	6
	27-60	A	17.1	0.41	6.1	24.4	<1	5.7	282.1	250	299	3
		B	19.5	0.57	7.6	31.8	<1	6.4	258.3	271	361	3
		Tot	19.2	0.55	7.4	31.0	<1	6.3	260.9	269	354	3
ZP3	0-9	A	56.0	2.64	19.9	92.8	2	17.0	110.6	276	433	12
		B	54.5	2.66	19.4	89.4	1	17.3	112.5	282	473	11
		Tot	54.6	2.66	19.5	89.8	1	17.2	112.2	282	469	11
	9-25	A	54.4	3.18	20.1	93.2	2	18.3	116.0	288	534	11
		B	60.4	2.95	20.5	91.7	1	18.3	113.2	275	441	11
		Tot	59.3	2.99	20.5	92.0	1	18.3	113.7	278	459	11
	25-40	A	55.2	3.58	21.3	98.2	1	17.3	114.9	276	422	11
		B	52.7	3.05	21.9	97.9	2	19.5	113.3	292	432	12
		Tot	52.9	3.08	21.9	97.9	2	19.3	113.4	291	431	12
	40-70	B	59.2	2.79	21.8	96.5	2	20.4	102.7	263	372	12
ZS	0-10	B	38.0	1.99	23.9	92.9	2	17.9	104.9	757	1010	5
SS1	0-10	A	33.3	3.41	17.0	105.7	2	6.8	197.3	626	2910	3
		B	43.9	9.11	30.4	203.9	3	5.2	56.8	201	1082	5
		Tot	39.5	6.76	24.8	163.4	3	5.9	114.8	376	1836	4
SS2	0-20	A	47.7	2.59	21.8	100.6	2	24.3	106.8	251	349	11
		B	58.2	2.55	22.7	100.8	2	25.6	100.8	247	341	11
		Tot	57.8	2.55	22.7	100.8	2	25.5	101.1	247	341	11
Zsed	0-10	B	42.2	1.03	14.3	54.6	<1	25.1	104.1	218	654	8

Table 2.5. Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Zeïda mining area and total amounts (A + B)

Sample code	Depth	Fraction	Y	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
	cm		*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
ZC	0-20	A	16.8	3.00	96.6	2.6	81	8.4	0.6	57.4	2.8	1.0
		B	17.7	3.49	105.5	2.9	91	8.6	0.6	61.5	3.4	1.5
		Tot	17.5	3.37	103.4	2.9	88	8.5	0.6	60.5	3.3	1.4
ZT	0-20	B	15.6	0.75	35.7	1.4	33	6.6	1.0	4.9	2.3	3.0
ZP1	0-6	A	19.9	1.96	58.9	1.5	58	10.5	0.4	28.0	3.1	1.1
		B	19.4	2.89	91.4	2.6	95	9.9	0.4	42.3	10.1	1.3
		Tot	19.6	2.54	79.3	2.2	81	10.1	0.4	37.0	7.5	1.2
	6-36	A	19.6	2.30	72.3	2.2	70	9.8	0.4	29.0	4.3	1.2
		B	16.9	2.77	83.4	2.4	81	9.4	0.5	39.3	7.1	1.3
		Tot	18.0	2.59	79.2	2.3	77	9.5	0.5	35.4	6.0	1.3
	36-52	A	29.4	2.71	78.3	2.2	80	12.3	0.5	37.0	8.6	2.4
		B	23.8	3.02	96.4	2.7	72	11.8	0.5	43.5	5.2	1.9
		Tot	25.7	2.92	90.2	2.5	75	12.0	0.5	41.3	6.3	2.1
ZP2	0-10	A	8.0	0.99	26.6	0.9	35	2.3	0.2	23.2	0.6	0.3
		B	11.2	2.03	47.7	1.3	65	4.2	0.4	40.3	1.0	0.6
		Tot	10.4	1.78	42.5	1.2	58	3.8	0.4	36.1	0.9	0.5
	10-27	A	10.5	1.18	31.5	0.8	39	3.3	0.2	27.2	0.8	0.3
		B	10.9	2.13	51.3	1.2	60	4.9	0.4	43.7	3.5	0.5
		Tot	10.8	1.93	47.1	1.1	56	4.5	0.4	40.2	2.9	0.5
	27-60	A	5.1	0.92	23.0	0.5	31	1.9	0.2	22.1	0.5	0.2
		B	6.2	1.17	28.0	0.8	40	2.6	0.2	27.3	0.6	0.7
		Tot	6.0	1.14	27.4	0.8	39	2.5	0.2	26.7	0.6	0.7
ZP3	0-9	A	18.8	3.77	81.6	2.2	96	11.5	0.6	62.0	0.9	0.9
		B	18.0	3.81	78.0	2.3	92	11.9	0.6	67.1	0.9	1.0
		Tot	18.1	3.81	78.5	2.3	93	11.8	0.6	66.4	0.9	1.0
	9-25	A	19.1	3.74	77.0	2.3	95	11.2	0.6	66.0	0.9	1.0
		B	18.0	3.84	78.7	2.4	94	11.6	0.6	58.7	0.9	0.9
		Tot	18.2	3.82	78.4	2.4	94	11.6	0.6	60.1	0.9	0.9
	25-40	A	17.0	3.56	79.4	2.1	93	12.8	0.6	61.0	0.8	0.9
		B	20.3	3.90	86.7	2.5	91	11.8	0.6	62.8	1.0	0.9
		Tot	20.1	3.88	86.3	2.5	91	11.8	0.6	62.7	1.0	0.9
	40-70	B	19.4	3.87	93.8	2.6	98	12.4	0.6	64.9	1.0	1.0
ZS	0-10	B	15.5	1.81	50.2	1.5	60	7.5	0.6	39.2	1.8	1.3
SS1	0-10	A	14.5	0.99	34.6	1.0	29	5.1	0.4	16.0	1.1	1.2
		B	14.7	1.87	57.8	1.8	45	10.0	0.8	24.1	1.2	1.5
		Tot	14.6	1.51	48.2	1.5	39	7.9	0.6	20.8	1.2	1.4
SS2	0-20	A	19.9	3.90	78.3	2.2	92	12.4	0.6	65.0	1.0	0.8
		B	18.5	3.89	95.1	2.4	96	11.8	0.7	63.7	1.0	1.0
		Tot	18.6	3.89	94.4	2.4	96	11.9	0.7	63.8	1.0	1.0
Zsed	0-10	B	12.6	2.60	67.4	2.0	73	5.9	0.5	47.4	1.5	0.7

Table 2.5. Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Zeïda mining area and total amounts (A + B)

Sample code	Depth	Fraction	Mn	Fe	Co	Ni	Cu	Ag	Zn	Cd	La
	cm		*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
ZC	0-20	A	2030	30.83	7.7	23.4	13.0	0.3	73	0.3	29.4
		B	2201	34.40	7.9	23.6	18.4	0.3	82	0.2	33.6
		Tot	2160	33.53	7.8	23.6	17.1	0.3	79	0.2	32.6
ZT	0-20	B	200	4.45	3.6	2.0	46.7	3.0	568	1.1	13.2
ZP1	0-6	A	2109	17.90	13.9	24.9	41.5	0.1	57	0.9	25.2
		B	5948	27.08	28.8	43.3	55.6	0.3	140	0.5	27.4
		Tot	4518	23.66	23.2	36.4	50.3	0.2	109	0.7	26.6
	6-36	A	3662	19.60	18.0	30.7	46.0	0.1	64	0.6	24.8
		B	4514	24.01	22.3	33.2	55.2	0.2	100	0.4	26.3
		Tot	4191	22.34	20.7	32.2	51.7	0.2	86	0.5	25.7
	36-52	A	4983	32.50	29.3	41.0	71.8	0.1	98	0.9	28.4
		B	3016	28.61	21.3	34.8	62.6	0.2	101	0.5	28.4
		Tot	3690	29.94	24.1	36.9	65.7	0.2	100	0.6	28.4
ZP2	0-10	A	278	9.38	6.3	12.2	13.5	0.1	35	0.4	10.4
		B	440	17.86	10.1	21.0	25.8	0.2	63	0.4	17.0
		Tot	400	15.77	9.2	18.8	22.8	0.2	56	0.4	15.4
	10-27	A	399	10.97	7.4	14.5	12.8	<0.1	44	0.5	12.0
		B	540	18.19	10.6	21.2	24.8	0.2	60	0.2	17.8
		Tot	510	16.65	9.9	19.8	22.2	0.2	57	0.3	16.5
	27-60	A	161	8.24	5.4	10.6	7.1	<0.1	26	0.2	7.8
		B	163	10.51	6.3	13.4	8.7	0.1	31	0.1	9.3
		Tot	162	10.26	6.2	13.1	8.5	0.1	31	0.1	9.1
ZP3	0-9	A	887	30.90	16.2	31.2	30.2	0.1	123	0.3	26.6
		B	918	32.41	17.8	32.9	32.6	0.1	129	0.3	28.2
		Tot	914	32.23	17.6	32.7	32.3	0.1	128	0.3	28.0
	9-25	A	885	31.30	15.9	30.1	31.2	0.1	117	0.5	26.3
		B	932	31.38	17.2	30.8	30.1	<0.1	116	0.4	26.2
		Tot	923	31.36	17.0	30.6	30.3	<0.1	117	0.4	26.2
	25-40	A	866	31.00	16.6	29.3	28.9	<0.1	111	0.4	25.3
		B	896	31.31	16.0	33.4	32.6	0.1	116	0.3	25.7
		Tot	894	31.29	16.0	33.2	32.4	0.1	115	0.3	25.7
	40-70	B	987	32.85	17.1	34.9	33.8	0.1	118	0.3	27.6
ZS	0-10	B	561	17.53	7.6	15.0	27.9	0.7	88	0.3	20.7
SS1	0-10	A	771	10.40	8.7	13.0	17.9	0.1	29	0.5	16.7
		B	476	15.98	7.5	13.6	20.8	0.2	40	0.1	21.7
		Tot	598	13.68	8.0	13.3	19.6	0.2	36	0.3	19.6
SS2	0-20	A	1079	31.20	19.3	33.8	35.2	<0.1	112	0.3	26.4
		B	1327	29.93	16.9	35.6	34.8	0.1	113	0.4	26.7
		Tot	1316	29.98	17.0	35.5	34.8	0.1	113	0.4	26.7
Zsed	0-10	B	1143	24.42	10.5	25.5	13.3	0.1	158	0.3	23.3

Table 2.5 (continued). Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Zeïda mining area and total amounts (A + B)

Sample code	Depth	Fraction	Ce	Th	U	Al	Sn	Pb	As	Sb	Bi
	cm		*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
ZC	0-20	A	55	8.3	4.2	54.0	1.7	43.3	14	3.5	0.3
		B	64	9.5	4.7	61.6	2.2	126.2	21	4.0	0.4
		Tot	62	9.2	4.6	59.8	2.1	106.1	19	3.9	0.4
ZT	0-20	B	24	8.2	4.5	46.8	1.8	4130.6	19	11.5	1.8
ZP1	0-6	A	37	4.0	2.3	20.8	0.5	213.8	20	0.9	0.1
		B	58	8.1	2.6	40.1	1.3	198.6	46	1.6	0.3
		Tot	50	6.5	2.5	32.9	1.0	204.3	37	1.3	0.2
	6-36	A	43	5.2	2.9	28.7	1.1	163.9	31	1.3	0.2
		B	55	7.3	2.9	38.7	1.2	182.7	31	1.4	0.3
		Tot	51	6.5	2.9	34.9	1.2	175.6	31	1.4	0.3
	36-52	A	47	5.9	4.0	31.2	1.1	220.0	26	1.4	0.2
		B	53	7.5	3.9	44.7	1.7	170.8	27	1.7	0.3
		Tot	51	6.9	4.0	40.1	1.5	187.6	27	1.6	0.3
ZP2	0-10	A	18	2.3	0.8	15.8	0.4	87.0	6	0.5	0.1
		B	34	4.1	1.2	29.6	0.9	166.4	8	1.2	0.3
		Tot	30	3.7	1.1	26.2	0.8	146.8	8	1.1	0.3
	10-27	A	21	2.7	1.1	19.5	0.6	90.1	4	0.6	0.2
		B	35	4.7	1.3	30.9	0.7	185.7	7	1.5	0.5
		Tot	32	4.3	1.3	28.5	0.7	165.4	6	1.3	0.4
	27-60	A	15	1.9	1.0	14.4	0.5	5.4	10	0.3	<0.1
		B	18	2.3	1.1	18.3	0.6	8.0	8	0.3	<0.1
		Tot	18	2.3	1.1	17.9	0.6	7.7	8	0.3	<0.1
ZP3	0-9	A	50	7.8	1.9	54.3	2.0	54.0	7	0.6	0.2
		B	52	8.2	1.8	57.4	2.1	51.5	7	0.6	0.2
		Tot	52	8.2	1.8	57.0	2.1	51.8	7	0.6	0.2
	9-25	A	50	8.9	2.0	57.8	2.0	52.6	8	0.6	0.2
		B	49	7.6	1.8	54.1	2.2	55.3	7	0.5	0.2
		Tot	49	7.8	1.9	54.8	2.2	54.8	7	0.5	0.2
	25-40	A	48	7.3	1.7	52.5	2.0	44.1	8	0.6	0.3
		B	50	7.8	1.7	54.5	1.9	48.1	8	0.6	0.2
		Tot	50	7.8	1.7	54.4	1.9	47.9	8	0.6	0.2
	40-70	B	50	7.6	1.8	55.3	2.0	31.9	7	0.6	0.2
ZS	0-10	B	38	7.0	2.0	33.4	1.0	1286.7	22	6.5	3.2
SS1	0-10	A	16.0	4.4	1.8	29.4	1.3	52.6	8	1.1	0.4
		B	24.1	8.7	2.3	51.9	1.9	56.7	10	1.2	0.5
		Tot	20.8	7.0	2.1	42.6	1.7	55.0	9	1.2	0.5
SS2	0-20	A	65.0	7.2	1.9	53.6	1.9	30.9	9	0.7	0.2
		B	63.7	8.1	2.0	54.2	2.4	31.2	9	0.6	0.4
		Tot	63.8	8.0	2.0	54.2	2.4	31.2	9	0.6	0.4
Zsed	0-10	B	45	6.5	1.7	45.0	1.2	38.3	10	0.7	0.2

Table 2.6. Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Mibladen mining area and total amounts (A + B)

Sample code	Depth	Fraction	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Sc
	cm		*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
MC1	0-20	A	7.9	0.36	3.3	14.8	2	91.1	177.2	1018	1065	3
		B	10.3	0.47	5.9	29.8	1	73.5	131.1	1251	833	4
		Tot	8.6	0.39	4.0	19.0	2	86.2	164.4	1083	1001	3
MC2	0-20	A	15.0	0.28	9.9	45.5	2	29.0	102.1	943	498	5
		B	16.5	0.44	13.2	64.1	2	39.1	118.8	287	3862	7
		Tot	15.9	0.37	11.8	56.4	2	34.9	111.8	561	2458	6
MT	0-20	B	16.2	0.27	3.5	17.1	<1	58.0	123.1	2188	590	2
MP1	0-15	B	15.9	0.84	9.2	31.2	<1	17.7	96.0	258	259	3
	15-45	B	22.6	1.04	12.4	44.8	<1	20.2	88.1	276	275	5
	45-75	B	17.2	0.88	10.3	36.9	<1	20.1	70.2	210	338	5
MP2	0-23	A	14.5	0.50	5.6	24.8	2	50.5	119.2	351	3375	4
		B	8.9	0.24	3.1	13.8	1	25.6	100.8	291	4037	2
		Tot	9.4	0.26	3.3	14.6	1	27.6	102.3	296	3986	2
	23-50	A	7.9	0.36	2.6	11.1	1	92.4	172.5	596	1201	2
		B	28.4	0.64	13.9	59.5	2	28.1	82.7	210	1403	10
		Tot	14.8	0.46	6.4	27.5	1	70.7	142.2	465	1270	5
	50-90	A	26.2	0.70	14.7	59.9	1	34.3	107.1	251	1371	10
		B	9.0	0.30	4.4	17.9	<1	37.7	111.2	740	1025	3
		Tot	20.7	0.57	11.4	46.5	1	35.4	108.4	407	1261	8
MP3	0-35	B	41.9	0.29	4.4	20.7	1	43.7	99.2	1920	667	2
	35-45	A	16.2	0.41	8.2	37.9	<1	43.3	142.2	1213	1309	4
		B	13.0	0.29	4.6	22.2	1	53.0	108.8	1744	944	3
		Tot	13.0	0.30	4.6	22.5	1	52.9	109.4	1735	950	3
	45-72	B	5.2	0.28	1.8	8.1	<1	54.8	115.0	2491	444	2
	72-92	B	19.7	1.37	9.6	47.0	1	44.1	97.3	1231	611	5
	92-150	B	7.3	0.77	3.0	12.3	<1	53.6	126.5	2076	435	2
SS	0-10	B	32.0	6.18	23.4	69.3	4	11.4	117.4	1144	1815	7
	10-20	B	42.3	5.83	35.1	106.6	3	13.9	99.5	897	1357	8
SS3	0-10	B	23.4	1.31	11.4	42.5	1	7.4	266.5	367	249	7
SS4	0-10	B	26.9	1.49	15.6	58.7	1	16.0	147.7	346	790	5
SS5	0-10	A	9.7	0.28	4.5	13.8	<1	7.5	291.4	283	395	2
		B	27.4	0.88	13.8	56.6	<1	12.9	67.2	187	375	6
		Tot	25.6	0.81	12.8	52.2	<1	12.3	90.5	197	377	6
	10-20	A	20.3	0.61	10.9	44.1	<1	11.9	166.9	240	348	6
		B	25.1	0.81	13.5	58.7	<1	13.3	78.8	211	425	7
		Tot	24.8	0.80	13.4	57.9	<1	13.2	83.6	213	421	7
SS6	0-10	A	9.2	0.30	4.0	11.1	<1	11.4	305.1	281	115	2
		B	24.1	1.26	11.9	42.3	<1	14.7	104.1	221	318	4
		Tot	21.8	1.11	10.6	37.5	<1	14.2	135.4	231	286	4
SS7	0-15	B	57.8	2.14	25.0	110.2	2	19.1	64.8	174	557	15
SS8	0-5	A	65.0	2.01	17.2	74.2	3	4.2	173.6	726	6394	9
		B	87.6	3.93	19.6	69.5	3	5.9	61.5	284	4377	8
		Tot	83.6	3.59	19.2	70.3	3	5.6	81.3	362	4734	8
sed	0-5	A	26.3	3.04	19.9	66.5	2	10.4	151.8	416	492	6
		B	30.9	2.61	17.4	63.9	1	11.1	145.4	394	490	7
		Tot	30.2	2.68	17.8	64.3	1	11.0	146.4	397	490	7

Table 2.6. Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Mibladen mining area and total amounts (A + B)

Sample code	Depth	Fraction	Y	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
	cm		*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
MC1	0-20	A	5.5	0.75	20.0	0.6	47	3.0	0.2	20.9	3.5	2.2
		B	6.3	1.42	32.1	1.0	67	5.3	0.3	36.4	3.9	3.2
		Tot	5.7	0.94	23.4	0.7	52	3.7	0.2	25.2	3.6	2.5
MC2	0-20	A	8.3	1.64	39.7	1.1	56	3.6	0.3	28.6	2.0	0.9
		B	11.9	2.46	66.2	1.8	83	5.7	0.4	39.4	2.6	1.1
		Tot	10.4	2.12	55.1	1.5	72	4.8	0.4	34.9	2.4	1.0
MT	0-20	B	4.4	0.66	14.5	0.5	28	2.4	0.2	8.6	2.2	1.6
MP1	0-15	B	8.9	1.46	37.6	1.0	47	4.1	0.2	22.2	1.1	0.3
	15-45	B	11.7	2.02	57.3	1.7	50	5.0	0.3	35.4	1.3	0.6
	45-75	B	9.9	1.71	46.3	1.3	46	4.1	0.2	23.2	1.1	0.4
MP2	0-23	A	6.7	1.16	28.5	0.9	50	5.0	0.2	31.4	4.1	1.5
		B	4.5	0.65	16.1	0.6	43	3.0	0.2	19.5	3.7	0.5
		Tot	4.6	0.69	17.1	0.6	43	3.2	0.2	20.4	3.8	0.6
	23-50	A	4.9	0.64	14.5	0.5	46	2.1	0.2	15.9	4.0	8.0
		B	10.7	3.22	81.2	2.6	105	12.1	0.8	61.1	2.1	3.6
		Tot	6.8	1.51	37.0	1.2	66	5.5	0.4	31.2	3.3	6.5
	50-90	A	11.2	3.28	73.9	2.5	104	11.6	0.7	61.1	2.3	3.7
		B	5.4	0.98	22.4	0.7	54	3.7	0.2	26.3	6.2	1.0
		Tot	9.3	2.55	57.5	1.9	88	9.1	0.6	50.0	3.5	2.8
MP3	0-35	B	6.5	0.80	18.2	0.5	65	1.9	0.2	16.1	4.3	2.1
	35-45	A	7.5	1.65	38.5	1.2	62	3.9	0.3	34.1	5.5	2.4
		B	5.7	1.10	26.4	0.7	48	2.4	0.1	22.3	8.3	1.9
		Tot	5.7	1.10	26.6	0.7	48	2.5	0.1	22.5	8.3	1.9
	45-72	B	4.5	0.49	15.6	0.5	24	1.3	<0.1	11.0	1.9	0.8
	72-92	B	7.7	2.06	48.7	1.4	90	5.4	0.3	35.2	9.6	3.7
	92-150	B	5.2	0.82	22.3	0.6	31	2.0	0.1	14.0	3.3	0.9
SS	0-10	B	33.7	10.75	246.5	4.6	421	136.2	2.1	148.7	14.8	8.3
	10-20	B	32.6	9.38	232.4	4.0	344	107.8	1.5	112.0	11.5	6.7
SS3	0-10	B	12.2	1.99	45.5	1.2	60	9.0	0.5	39.1	0.6	2.2
SS4	0-10	B	10.0	2.03	45.4	1.4	76	9.8	0.6	39.0	1.5	1.1
SS5	0-10	A	14.2	0.68	20.7	0.6	25	2.1	0.1	18.0	1.0	0.2
		B	15.7	2.41	69.9	1.9	62	8.1	0.3	36.3	1.4	0.6
		Tot	15.6	2.23	64.8	1.8	59	7.4	0.3	34.4	1.4	0.6
	10-20	A	17.1	1.92	57.7	1.7	59	6.3	0.3	30.0	1.3	0.4
		B	15.6	2.57	69.1	2.0	69	8.4	0.3	39.0	1.4	0.6
		Tot	15.7	2.53	68.5	2.0	68	8.3	0.3	38.5	1.4	0.6
SS6	0-10	A	8.7	0.60	17.0	0.4	21	2.1	<0.1	18.0	1.0	0.2
		B	12.6	2.43	71.7	2.0	44	9.3	0.4	33.2	1.0	0.6
		Tot	12.0	2.15	63.2	1.8	41	8.1	0.3	30.8	1.0	0.5
SS7	0-15	B	23.0	4.42	103.8	3.3	122	16.8	0.8	81.5	1.6	1.5
SS8	0-5	A	10.8	3.17	51.6	1.6	77	9.5	0.5	35.0	1.2	11.8
		B	14.2	4.14	78.3	2.3	80	13.1	0.7	45.2	1.2	9.8
		Tot	13.6	3.97	73.6	2.2	80	12.4	0.7	43.4	1.2	10.2
sed	0-5	A	15.7	3.42	84.1	2.2	101	30.3	0.6	38.0	5.3	2.7
		B	16.2	3.70	91.1	2.4	96	29.5	0.6	43.3	3.2	2.6
		Tot	16.1	3.65	90.0	2.4	97	29.6	0.6	42.5	3.5	2.6

Table 2.6. Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Mibladen mining area and total amounts (A + B)

Sample code	Depth	Fraction	Mn	Fe	Co	Ni	Cu	Ag	Zn	Cd	La
	cm		*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
MC1	0-20	A	2485	10.87	15.7	34.1	211.3	0.9	304	2.2	8.8
		B	2140	13.54	11.8	26.5	65.4	2.3	632	3.8	11.1
		Tot	2389	11.61	14.7	32.0	170.7	1.3	395	2.7	9.5
MC2	0-20	A	1667	20.36	7.8	16.8	712.4	38.2	44	0.3	13.7
		B	1819	26.04	10.1	21.0	59.0	0.4	81	0.3	20.5
		Tot	1755	23.67	9.1	19.2	331.7	16.2	66	0.3	17.7
MT	0-20	B	1781	8.28	9.4	15.0	78.0	1.4	1063	5.1	6.6
MP1	0-15	B	475	11.21	8.4	14.3	13.0	0.1	46	0.4	13.0
	15-45	B	489	15.95	8.5	19.2	16.9	<0.1	66	0.4	17.3
	45-75	B	494	13.40	8.2	16.7	13.8	<0.1	54	0.4	14.7
MP2	0-23	A	1589	19.63	9.6	20.5	412.5	2.7	91426	404.5	11.3
		B	808	19.56	5.9	13.1	364.5	3.5	189342	1071.0	7.3
		Tot	869	19.56	6.2	13.7	368.3	3.5	181705	1019.0	7.6
	23-50	A	2182	11.75	9.4	17.2	359.1	1.3	9053	55.9	7.4
		B	527	31.66	4.6	13.1	20.9	0.2	2227	4.8	26.7
		Tot	1623	18.48	7.8	15.8	244.8	0.9	6746	38.6	13.9
	50-90	A	794	32.29	5.6	16.4	23.3	0.2	1868	14.0	27.8
		B	1103	20.12	6.5	15.2	362.7	5.7	793	731.2	9.1
		Tot	893	28.41	5.9	16.0	131.5	2.0	1525	242.8	21.8
MP3	0-35	B	1307	8.84	13.2	17.8	348.0	1.8	3083	16.2	9.0
	35-45	A	1227	13.45	9.8	32.4	65.2	3.2	125	1.7	13.3
		B	1855	10.04	10.8	27.7	70.7	3.3	215	2.2	7.6
		Tot	1845	10.10	10.7	27.8	70.6	3.3	214	2.2	7.7
	45-72	B	1651	5.70	9.9	16.9	34.6	0.6	223	3.6	3.9
	72-92	B	1661	15.57	11.9	33.4	76.0	4.4	123	1.5	12.8
	92-150	B	1269	6.61	7.3	13.8	32.5	1.3	116	2.7	5.3
SS	0-10	B	2154	52.44	23.8	52.2	24.5	0.3	174	0.8	100.9
	10-20	B	2065	49.10	23.6	58.3	29.1	0.1	181	0.8	99.3
SS3	0-10	B	885	22.78	12.4	17.8	19.7	0.1	84	0.5	22.7
SS4	0-10	B	520	22.78	7.7	16.2	14.7	0.1	64	0.5	18.5
SS5	0-10	A	227	6.90	3.9	7.1	13.5	0.2	25	0.8	12.1
		B	435	18.94	11.7	22.0	34.5	0.1	50	0.2	21.0
		Tot	414	17.69	10.9	20.4	32.3	0.1	48	0.3	20.0
	10-20	A	422	18.20	11.4	21.8	30.2	0.1	50	0.5	20.2
		B	433	20.90	12.7	22.8	37.6	0.1	49	0.3	21.9
		Tot	432	20.75	12.6	22.7	37.2	0.1	49	0.3	21.8
SS6	0-10	A	187	4.90	2.2	6.5	3.9	0.2	18	0.5	9.8
		B	382	14.89	8.6	16.7	14.2	0.1	39	0.2	19.8
		Tot	352	13.33	7.6	15.1	12.6	0.1	36	0.2	18.3
SS7	0-15	B	1022	41.77	18.3	42.3	41.4	0.1	132	0.7	40.2
SS8	0-5	A	272	30.50	7.7	8.2	19.2	0.2	52	0.2	35.3
		B	591	31.43	12.2	22.0	24.3	0.2	77	0.3	36.6
		Tot	535	31.27	11.4	19.6	23.4	0.2	73	0.3	36.3
sed	0-5	A	592	21.80	13.0	20.7	20.6	<0.1	56	0.3	34.9
		B	602	23.68	13.6	22.8	21.8	<0.1	58	0.2	34.6
		Tot	601	23.38	13.5	22.4	21.6	<0.1	58	0.2	34.6

Table 2.6 (continued). Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Mibladen mining area and total amounts (A + B)

Sample code	Depth	Fraction	Ce	Th	U	Al	Sn	Pb	As	Sb	Bi
	cm		*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
MC1	0-20	A	14	2.0	1.1	10.7	20.5	3709.4	34	14.8	0.2
		B	20	3.1	1.6	22.3	0.6	7050.7	24	6.6	0.1
		Tot	16	2.3	1.3	13.9	15.0	4638.3	31	12.5	0.2
MC2	0-20	A	27	4.1	1.7	26.9	0.9	10083.2	5	16.6	0.2
		B	39	5.9	1.3	39.2	1.2	1155.3	6	1.2	0.1
		Tot	34	5.2	1.5	34.1	1.1	4128.1	6	7.6	0.1
MT	0-20	B	11	1.4	1.7	10.0	0.4	7116.2	16	9.3	0.1
MP1	0-15	B	25	3.7	0.9	18.8	0.6	41.7	2	0.2	0.1
	15-45	B	36	5.5	1.4	28.6	0.7	72.8	4	0.4	0.1
	45-75	B	29	4.6	1.1	24.7	0.7	34.5	4	0.3	<0.1
MP2	0-23	A	18	3.1	2.5	18.2	2.9	9143.6	124	8.5	0.2
		B	11	2.1	2.3	10.8	0.9	13629.5	274	7.8	0.1
		Tot	12	2.2	2.3	11.4	1.1	13279.6	262	7.9	0.1
	23-50	A	11	1.6	1.3	8.6	31.0	5030.7	31	13.2	0.2
		B	42	9.1	1.6	51.7	2.3	21679.7	12	2.3	0.2
		Tot	22	4.1	1.4	23.2	21.3	10658.1	25	9.5	0.2
	50-90	A	45	9.1	1.7	47.9	2.1	412.0	12	2.3	0.2
		B	15	2.4	2.4	14.3	0.8	315.7	201	11.4	0.1
		Tot	36	7.0	2.0	37.2	1.7	381.3	73	5.2	0.2
MP3	0-35	B	19	1.4	2.0	12.1	0.8	6561.4	18	11.3	1.7
	35-45	A	25	3.2	2.4	27.9	1.3	13389.0	21	11.1	0.1
		B	16	1.4	1.8	18.7	0.7	14263.6	19	8.9	<0.1
		Tot	16	1.4	1.8	18.8	0.7	14263.6	19	9.0	<0.1
	45-72	B	9	0.9	1.0	7.0	0.3	2779.5	11	4.4	<0.1
	72-92	B	27	3.6	2.8	34.8	1.1	17205.4	23	13.6	0.1
	92-150	B	12	1.3	1.1	9.3	0.2	5176.2	10	3.9	<0.1
SS	0-10	B	148	20.6	4.7	55.8	2.0	49.0	19	1.5	0.3
	10-20	B	146	18.4	3.8	60.4	2.2	46.5	19	1.4	0.3
SS3	0-10	B	39	6.1	1.2	28.4	2.5	56.3	8	0.5	0.1
SS4	0-10	B	31	5.6	1.4	29.9	0.9	57.6	1.5	0.4	0.1
SS5	0-10	A	17	1.8	1.2	10.0	0.5	14.9	4	0.2	0.1
		B	40	5.9	1.4	30.7	1.0	27.7	7	0.4	0.2
		Tot	38	5.5	1.4	28.6	1.0	26.4	7	0.4	0.2
	10-20	A	36	5.1	1.4	26.1	0.8	26.8	6	0.3	0.1
		B	42	6.1	1.4	32.1	0.9	28.4	9	0.4	0.2
		Tot	42	6.0	1.4	31.8	0.9	28.3	9	0.4	0.2
SS6	0-10	A	14	1.6	0.9	7.8	0.1	5.5	3	0.1	<0.1
		B	35	4.9	1.3	25.3	0.8	16.8	6	0.3	<0.1
		Tot	32	4.4	1.2	22.6	0.7	15.0	6	0.3	<0.1
SS7	0-15	B	73	10.7	2.0	79.7	2.6	96.5	13	0.8	0.3
SS8	0-5	A	64	7.1	1.9	51.7	2.6	28.7	12	1.3	0.1
		B	69	9.1	1.8	54.0	2.3	36.6	11	1.4	0.3
		Tot	68	8.8	1.8	53.6	2.4	35.2	11	1.4	0.3
sed	0-5	A	52	8.1	1.5	36.4	0.9	18.7	7	0.5	0.2
		B	54	8.2	1.7	35.7	0.9	19.2	7	0.5	0.2
		Tot	54	8.2	1.7	35.8	0.9	19.2	7	0.5	0.2

Table 2.7. Total element content in the skeleton (fraction A: > 2 mm) and fine earth (fraction B: < 2 mm) of the wastes, soils and sediments from Aouli mining area and total amounts (A + B)

Sample code	Depth	Fraction	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Sc
	cm		*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
AC	0-20	A	62.3	0.31	5.6	26.3	1	5.5	19.5	604	580	2
		B	59.7	2.20	18.9	75.4	2	6.8	42.1	268	3821	7
		Tot	62.1	0.47	6.8	30.4	1	5.6	21.4	576	852	2
AT	0-20	B	17.8	3.17	10.1	46.0	1	29.9	112.2	1489	341	4
Ased	0-20	B	33.1	8.24	19.0	82.0	2	11.5	135.5	730	2519	5

Sample code	Depth	Fraction	Y	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
	cm		*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
AC	0-20	A	12.3	0.64	11.7	0.5	20	2.2	0.1	8.2	0.4	1.3
		B	14.6	2.51	65.5	1.9	59	8.9	0.6	31.1	1.4	2.1
		Tot	12.5	0.79	16.2	0.6	23	2.8	0.1	10.1	0.5	1.4
AT	0-20	B	8.3	1.76	37.9	1.0	44	5.6	0.3	21.1	2.3	1.7
Ased	0-20	B	11.3	2.86	43.6	1.4	59	18.0	1.1	32.8	2.4	3.1

Sample code	Depth	Fraction	Mn	Fe	Co	Ni	Cu	Ag	Zn	Cd	La
	cm		*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
AC	0-20	A	1943	9.18	6.7	7.5	1066.6	6.4	297	1.8	25.5
		B	2642	26.83	9.7	18.2	223.0	4.6	248	1.0	37.5
		Tot	2002	10.66	6.9	8.4	995.7	6.2	293	1.7	26.5
AT	0-20	B	1027	15.04	9.4	18.6	52.5	0.7	508	2.7	17.9
Ased	0-20	B	861	24.64	9.0	14.4	20.7	0.2	164	0.8	25.3

Sample code	Depth	Fraction	Ce	Th	U	Al	Sn	Pb	As	Sb	Bi
	cm		*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
AC	0-20	A	41	1.9	1.4	13.6	40.4	3474.7	6	9.9	18.7
		B	61	8.3	3.1	38.4	2.1	2258.7	14	4.7	13.6
		Tot	43	2.5	1.6	15.7	37.2	3372.5	7	9.4	18.2
AT	0-20	B	37	5.1	1.1	23.6	1.1	2360.4	8	1.8	0.3
Ased	0-20	B	40	6.6	1.5	37.8	1.5	783.3	10	0.8	0.2

Table 2.8. PTMs concentration limits imposed by the Italian Ministry of Environment for soils based on the use (DM 152/06).

PTMs	*Soils for public, residential and private use (mg kg^{-1})*	*Soils for commercial and industrial use (mg kg^{-1})*
As	20	50
Be	2	10
Cd	2	15
Co	20	250
Cr	150	800
Cu	120	600
Hg	1	5
Ni	120	500
Pb	100	1000
Sb	10	30
Se	3	15
Sn	1	350
Tl	1	10
V	90	250
Zn	150	1500

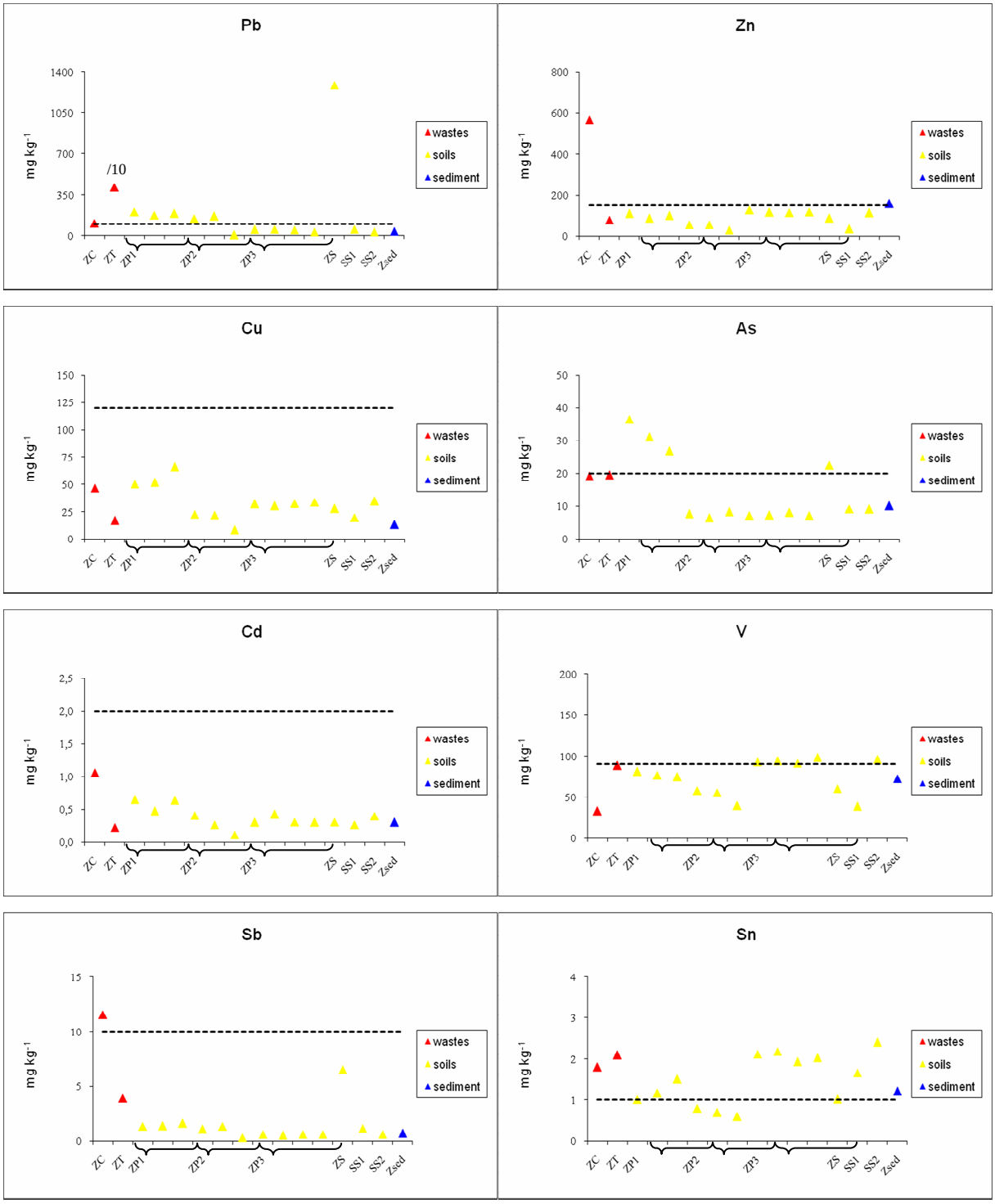

Figure 2.4. Main PTMs concentrations in the samples from Zeïda area; dotted lines indicate the limit imposed by the Italian Ministry of Environment (DM 152/06) for soils.

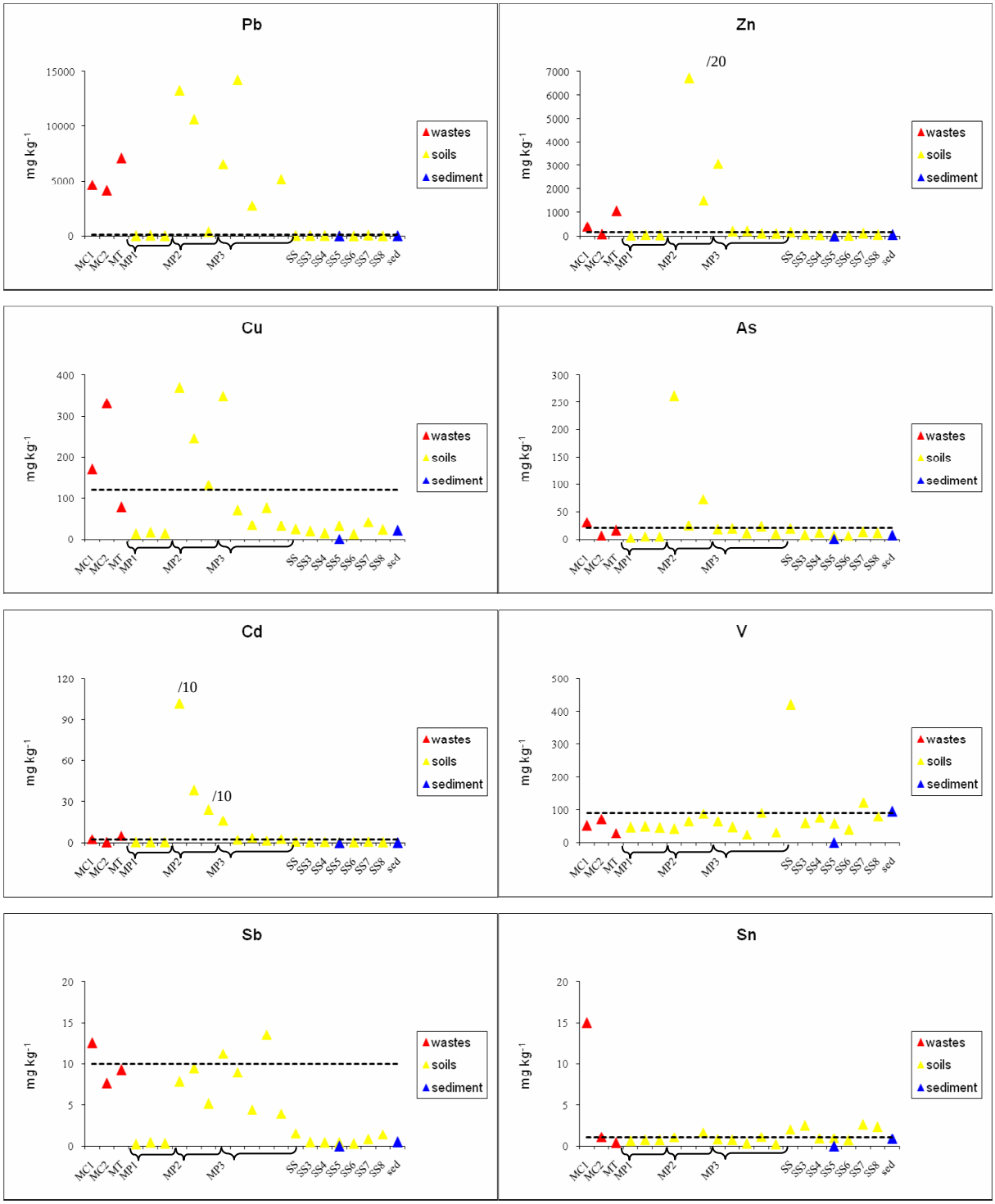

Figure 2.5. Main PTMs concentrations in the samples from Mibladen area; dotted lines indicate the limit imposed by the Italian Ministry of Environment (DM 152/06) for soils.

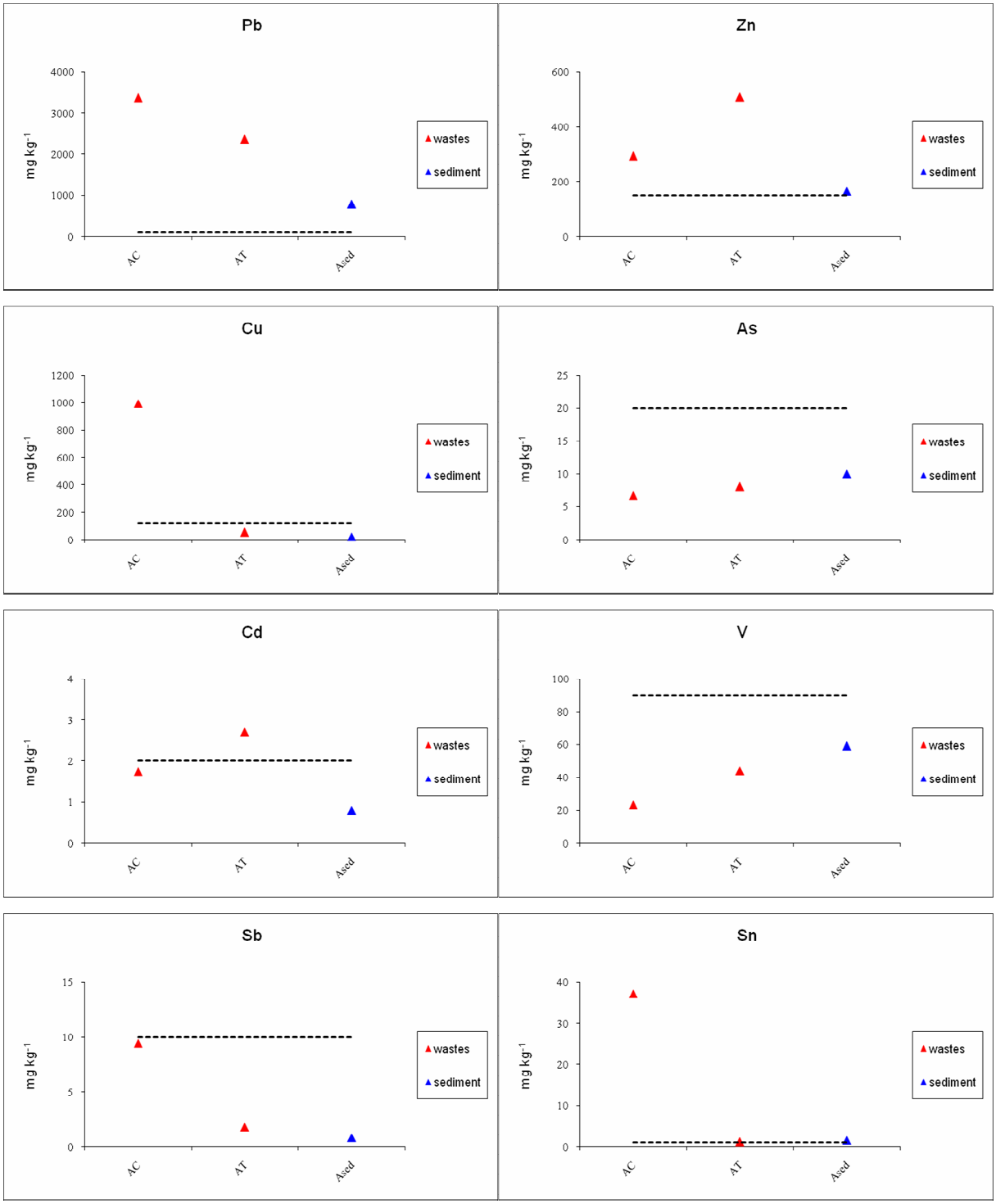

Figure 2.6. Main PTMs concentrations in the samples from Aouli area; dotted lines indicate the limit imposed by the Italian Ministry of Environment (DM 152/06) for soils.

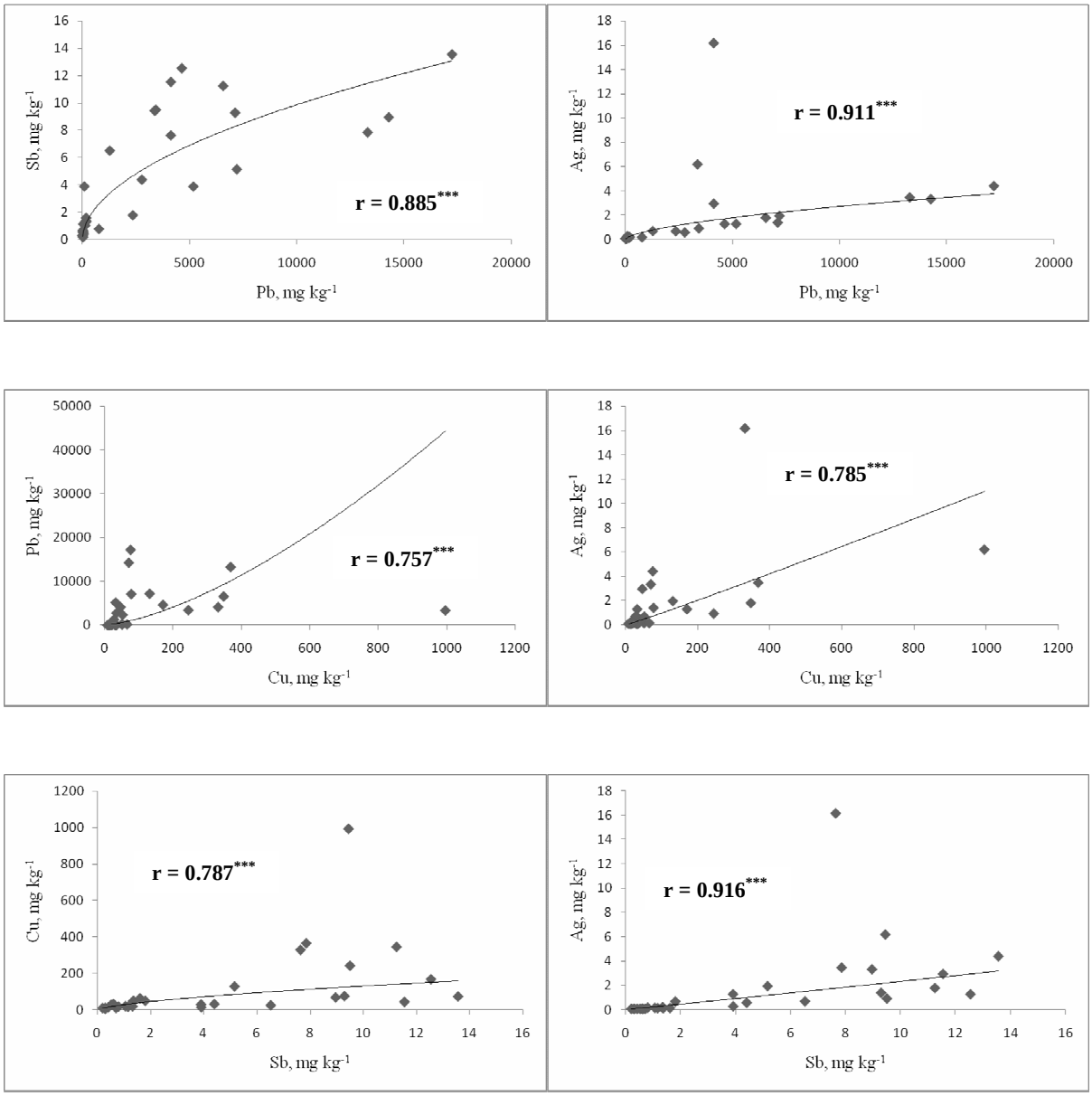

Figure 2.7. Relationships between Pb, Sb, Ag and Cu concentration in all samples from Upper Moulouya mining district (*** level of significance, $p < 0.001$).

Table 2.9. Individual amounts of metal contaminants in the clay fraction (< 2 µm) expressed in mg of metal kg^{-1} of < 2 µm fraction of selected wastes, soils and sediments

Sample code	Depth	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Sc	Y	Ti	Zr
	cm	*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*
ZT	0-20	109.4	0.335	2.93	152.3	7	0.53	0.91	2852	2015	3	28.1	2.491	75.5
ZS	0-10	62.7	0.072	1.85	82.5	3	1.83	8.92	677	8470	11	15.9	0.629	71.0
MC1	0-20	30.2	0.067	2.04	107.2	3	3.25	5.55	648	7637	11	12.4	0.474	97.5
MT	0-20	50.1	0.073	3.13	157.7	4	2.45	3.04	2776	2239	10	11.2	0.413	94.5
MP2	0-23	34.3	0.052	1.67	78.9	3	1.57	2.31	273	4968	9	14.0	0.382	87.0
AC	0-20	61.2	0.445	1.86	107.4	3	1.21	11.64	601	6554	9	14.9	0.669	53.9
Ased	0-20	87.9	0.285	3.19	158.5	7	1.18	0.52	162	3122	16	22.8	0.901	114.0

Sample code	Depth	Hf	V	Nb	Ta	Cr	Mo	W	Mn	Fe	Co	Ni	Cu	Ag
	cm	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
ZT	0-20	2.3	342	9.4	1.3	29	701.1	15.1	399	1.32	14.1	15.9	223.1	5.6
ZS	0-10	1.9	121	7.2	0.5	93	121.7	2.0	715	3.57	17.9	42.4	51.0	0.9
MC1	0-20	2.8	156	8.7	0.6	87	26.2	9.2	1320	3.36	16.3	57.7	108.7	1.9
MT	0-20	2.6	171	8.1	0.6	89	24.0	9.6	1110	3.10	20.1	77.8	383.6	10.0
MP2	0-23	2.4	138	7.7	0.6	93	33.2	6.2	1148	5.07	23.7	58.9	1121.4	6.7
AC	0-20	1.5	114	9.0	0.5	57	140.3	4.6	1256	3.85	20.6	39.6	50.6	1.0
Ased	0-20	2.9	180	13.6	0.9	93	136.3	6.6	4415	6.76	27.7	60.6	186.4	3.9

Sample code	Depth	Zn	Cd	La	Ce	Th	U	Al	Sn	Pb	As	Sb	Bi
	cm	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*g kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*
ZT	0-20	2785	2.4	23.9	51	13.4	10.2	6.74	7.5	10036	49	33.2	5.2
ZS	0-10	209	0.6	27.1	52	7.1	2.4	6.59	2.4	1526	20	6.3	2.8
MC1	0-20	774	3.2	28.3	51	7.9	3.1	7.40	3.1	4797	31	8.9	0.2
MT	0-20	3290	5.5	25.0	44	7.3	7.0	7.34	3.1	9993	53	40.1	0.7
MP2	0-23	181019	354.5	27.6	52	8.3	6.3	6.25	3.5	13281	285	21.1	0.5
AC	0-20	309	1.2	27.0	52	6.4	1.5	5.14	3.2	1535	12	1.8	0.4
Ased	0-20	555	1.9	47.3	90	13.1	4.3	9.54	4.3	1913	21	3.4	6.3

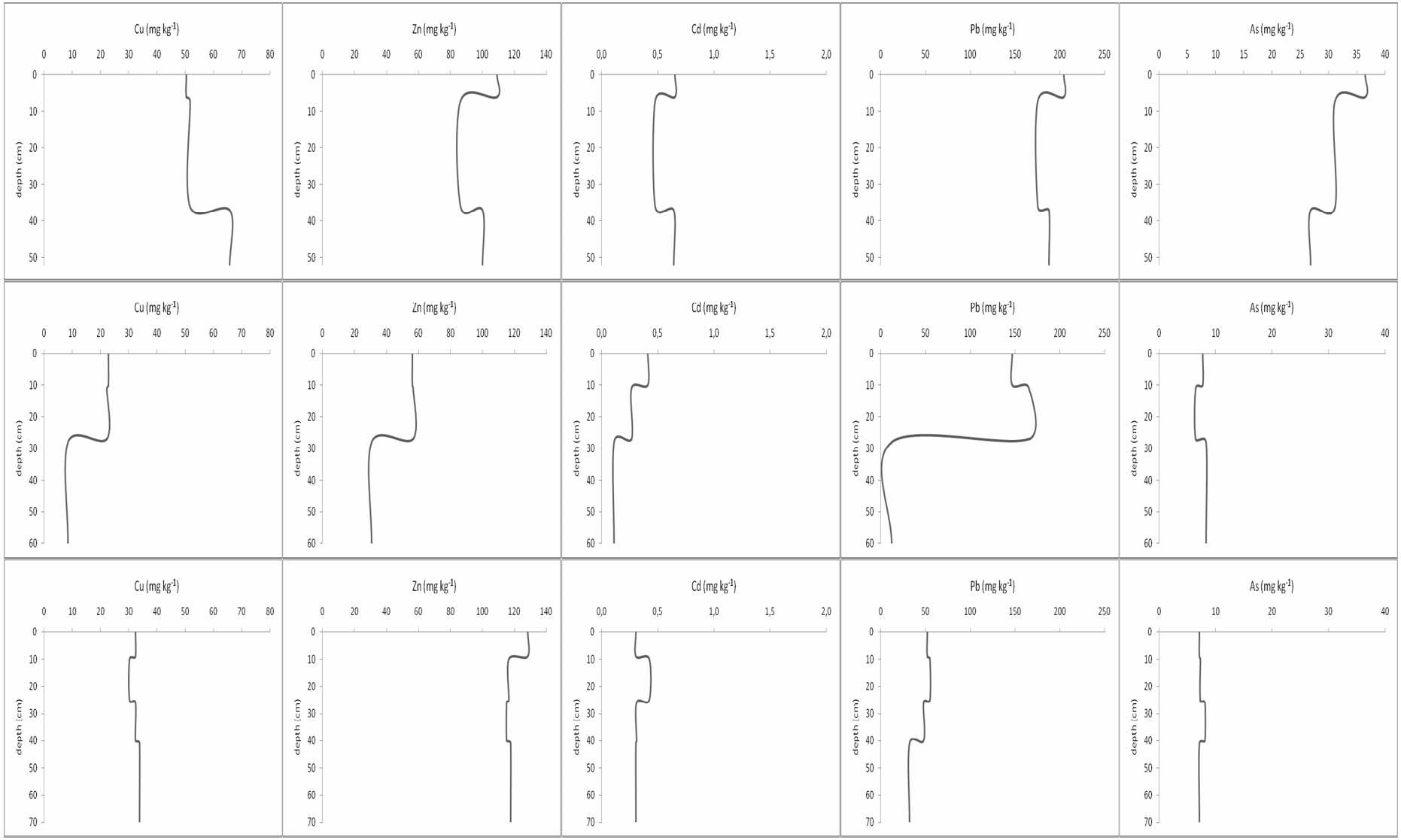

Figure 2.8. The vertical distribution of the total content of the main metal contaminants in soils from Zeïda.

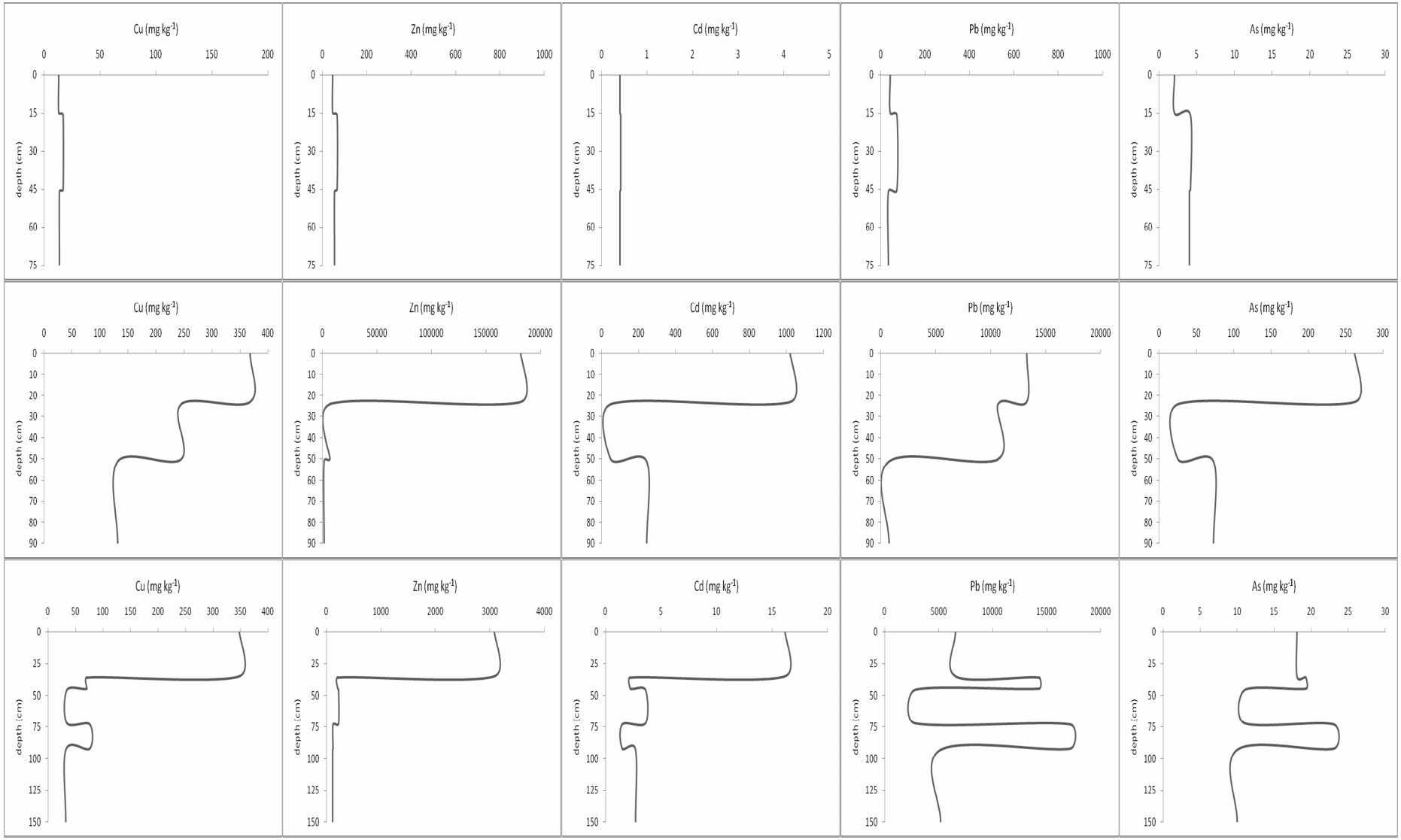

Figure 2.9. The vertical distribution of main metal contaminants in soils from Mibladen.

2.3.4. Total content of metal contaminants in the clay fraction (< 2 µm)

On the fine earth fraction separated from a selected number of wastes, soils and sediments, a particle-size fractionation (2 mm – 10 µm; 10 µm – 2 µm; < 2 µm) was carried out by centrifugation (Fig. 2.10). In the majority of the samples the 2 mm – 10 µm was the dominant fraction. The < 2 µm fraction was above 10% only in Zeïda tailings (16%), in MP2 (11%) and in the river sediment collected in Aouli (18%). The 10 µm – 2 µm fraction occurred in consistent amount only in the ZS sample (36%). The finest fractions can give indication about the contribution of waste and soil materials to $PM_{2.5}$ and PM_{10} for inhalation, while the coarsest fraction can adhere to the skin and be orally ingested.

The individual amounts of all analyzed elements in the clay fraction (< 2 µm), expressed in mg of metal kg^{-1} of < 2 µm fraction, are shown in Table 2.9. Elements are expected to increase in concentration with the decrease in particle-size. This can be attributed to the greater reactivity of the fine particles and to the accumulation of metals' precipitates in this fraction.

This trend for metal contaminants Pb, Zn, Cu, As, Cd, Sb, V and Sn is graphically shown in Fig. 2.11, where the < 2 µm fraction values are compared with the amounts of metal contaminants in the skeleton (if present) (∅ > 2 mm) and fine earth (∅ < 2 mm) of the same samples (values in Tables 2.5, 2.6, 2.7).

In the majority of the samples, but more pronounced in the tailings, the clay fraction was enriched in metal contaminants compared with fine earth and skeleton. For Pb and Zn the average content in tailings was Pb: 10015 mg kg^{-1} of clay fraction > 5623 mg kg^{-1} of fine earth; Zn: 3038 mg kg^{-1} of clay fraction > 815 mg kg^{-1} of fine earth. The other elements followed the same behaviour. In particular, the clay fraction from all analyzed materials had contents of As and V above regulatory levels indicating a contamination which did not occur in fine earth and skeleton [average values: As: 67 mg kg^{-1} of clay fraction > 51 mg kg^{-1} of fine earth = 50 mg kg^{-1} of skeleton; V: 175 mg kg^{-1} of clay fraction > 45 mg kg^{-1} of fine earth > 39 mg kg^{-1} of skeleton].

In coarse rock wastes (MC1 and AC) and in MP2 soil which was localized in the proximity of a big coarse waste dump, the content of metals in fine earth and skeleton was in several cases higher than that of the clay fraction; in particular, the highly contaminated MP2 sample had a fine earth more enriched in Cd (1019 mg kg^{-1}) than the clay fraction (355 mg kg^{-1}) and the skeleton (404 mg kg^{-1}). This is probably the consequence of the treatments of the ores which were depleted of the parts containing the economically important metals.

Among the other elements, they usually occurred in high concentrations in the clay fraction of most analyzed materials; in particular, Ni, Co and Cr always showed higher values in clay fraction than those in the coarser ones. When the overall average is considered, the content of Ni in each fraction was: 50 mg kg^{-1} of clay fraction > 15 mg kg^{-1} of fine earth > 9 mg kg^{-1} of skeleton; the content of Co in each fraction was: 20 mg kg^{-1} of clay fraction > 8 mg kg^{-1} of fine earth > 5 mg kg^{-1} of skeleton; the content of Cr in each fraction was: 77 mg kg^{-1} of clay fraction > 20 mg kg^{-1} of fine earth > 9 mg kg^{-1} of skeleton.

The contribution of the particles with diameter < 2 µm to the total concentration of metal contaminants in the fine earth is given in Table 2.10. The contribution was calculated multiplying the mg of metal kg^{-1} of < 2 µm fraction for the percentages of clay fraction in the < 2 mm soil.

Only in the tailings from Zeïda and in the river sediment from Aouli, the clay fraction contributed consistently to the total content of all metal contaminants in the fine earth (from 37% for Cd to 96% of V in ZT; from 22% for AS to 44% of Cu in Ased). In all other cases clay contribution never was above 25% and in the most contaminated samples (MC1, MT and AC) it was very low (below 7% for the main metal contaminants Pb and Zn). The clay contribution was also relevant for Pb and Sb in ZS soil sample (97 and 98%, respectively).

2.3.5 Pb and Zn bioavailability as assessed by 0.1M $CaCl_2$ extraction

The amounts of Pb and Zn extracted by 0.1M $CaCl_2$ from selected contaminated fine earths samples are given in Fig. 2.12. These amounts were always very low (Pb ranging from 0.5 mg kg^{-1} in ZP2 Ak to 4.2 mg kg^{-1} in ZT; Zn ranging from 0.02 mg kg^{-1} in ZP2 Ak to 7.3 mg kg^{-1} in MP2 Ck) and, with the exception of Pb in MP1 Ak, represented only a very small percentage (< 0.3%) of the total content of the fine earth.

Table 2.10. Concentration of metal contaminants in the clay fraction (< 2 µm) expressed as % of the respective total content in the fine earth of selected wastes, soils and sediments

Sample	Depth *(cm)*	V	Co	Cu	Zn	Cd	Sn	Pb	As	Sb
ZT	0-20	96	63	77	79	37	67	39	42	47
ZS	0-10	10	15	22	21	7	17	97	10	98
MC1	0-20	11	4	2	7	4	1	4	4	3
MT	0-20	10	3	8	5	2	12	2	5	7
MP2	0-23	21	25	20	6	2	21	7	7	17
AC	0-20	12	6	0	3	2	0	1	5	1
Ased	0-20	35	41	44	34	27	38	35	22	40

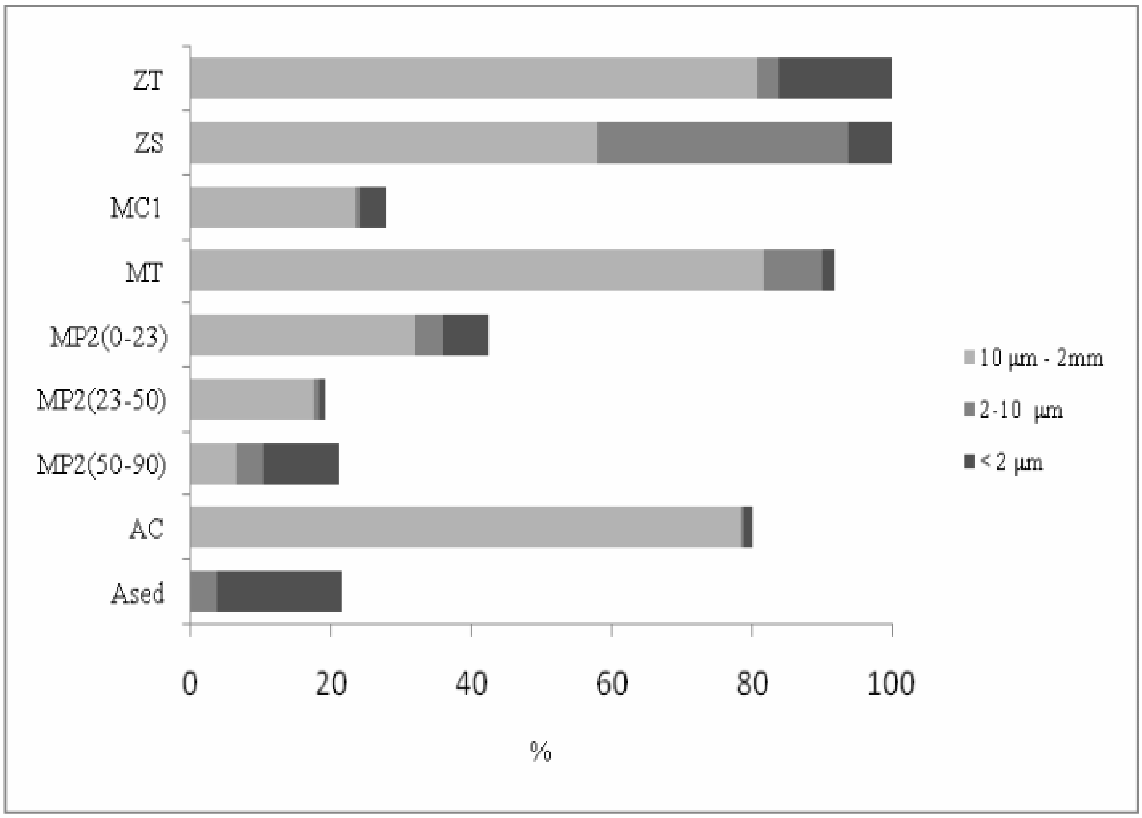

Figure 2.10. Particle-size fractionation of selected samples.

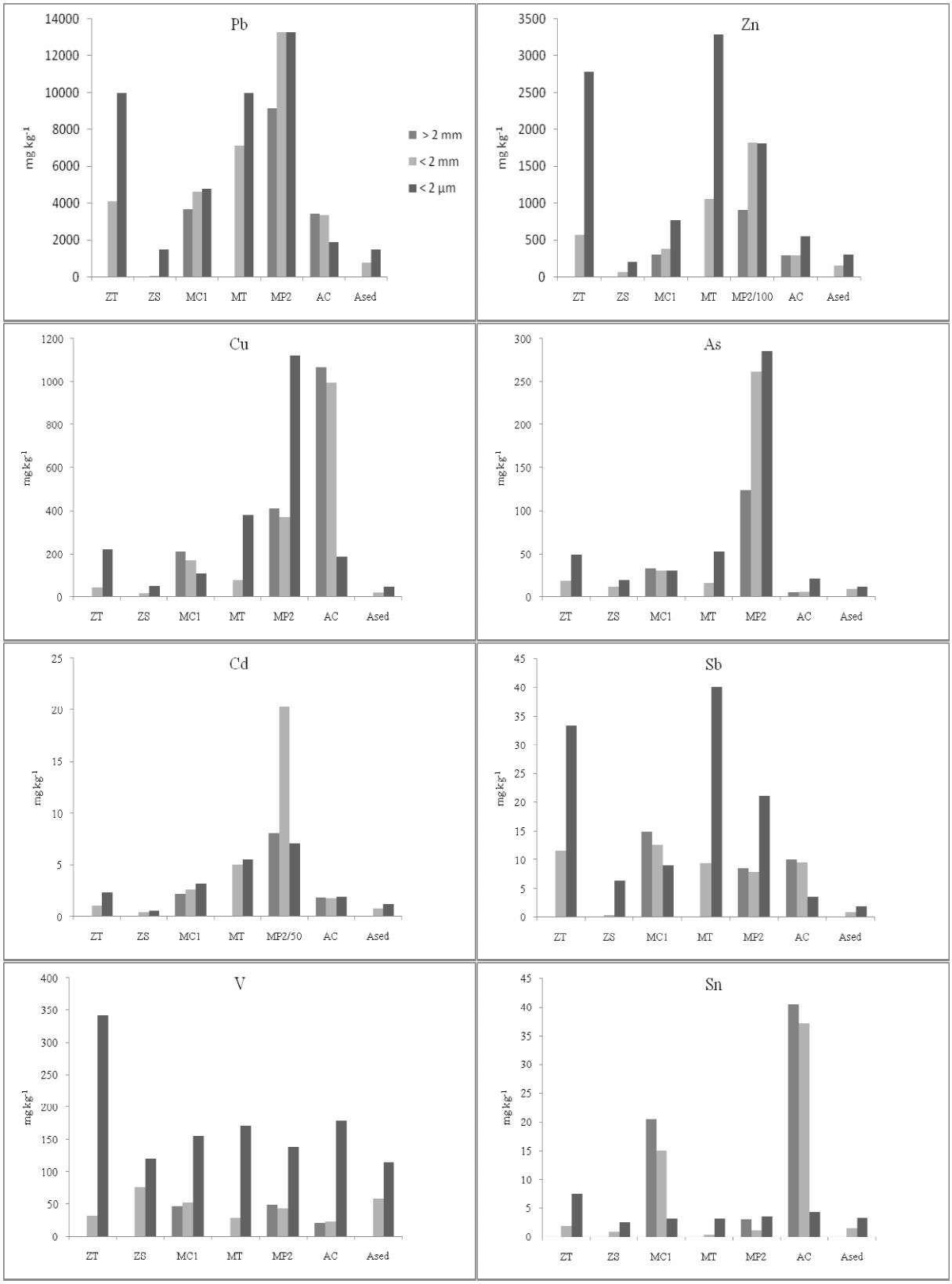

Fig. 2.11. Concentrations of main PTMs in the skeleton (> 2 mm), fine earth (< 2 mm) and clay fraction (< 2 µm) of selected samples.

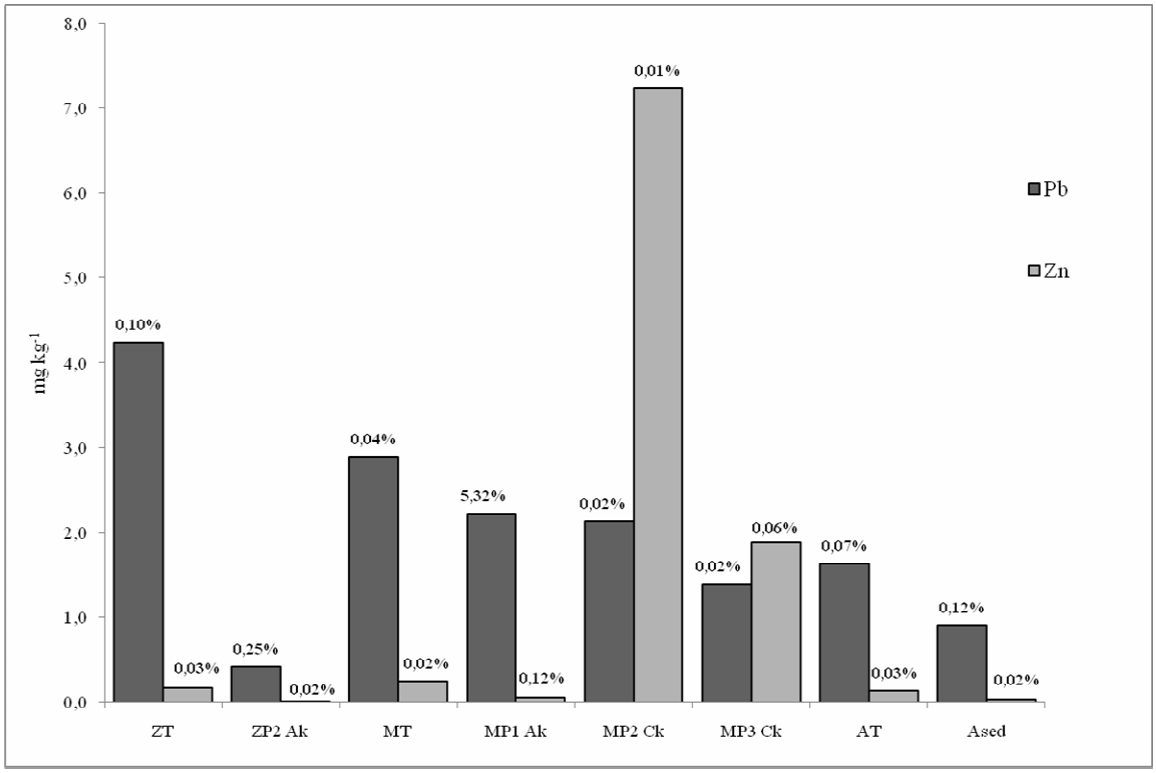

Figure 2.12. Amounts of Pb and Zn extracted by 0.1M $CaCl_2$ from selected contaminated fine earths samples.

CHAPTER 3

IMPACT OF PAST MINING ACTIVITY ON THE QUALITY OF RIVER WATER AND GROUNDWATER

3.1 Introduction

Mining activities have a significant influence on the quantity and quality of water resources in their surrounding environment (Schmiermund and Drozd, 1997; Cidu et al., 2009). Although water-quality related problems may arise during the phase of active mining, it is often the case that the most adverse impact is felt once exploitation of the mine has been discontinued (Banks at al., 1997).

The potential impact of mining works and their cessation on the quality of water resources is a primary concern in local communities. In many mining regions, even in some arid environments, pits may intercept groundwater, and require pumping during exploitation (Cidu et al., 2001). The rebound after the mine closure degrades the quality of groundwater and it may not be suitable for further uses (Gandy and Younger, 2007; Van Tonder et al., 2007).

The aim of this work was to characterize surface water and groundwater samples in order to evaluate the impact of past mining activity on the quality of the waters.

3.1.1 Moulouya River

The Moulouya basin represent a very important water potential, which can contain up to 1179 Mm^3/year (633 Mm^3/year moved by the High Moulouya), i.e. the 12% of the surface water reservoir of Morocco (D.G.H., 2003).

Before flowing toward the Mediterranean sea, Moulouya river receives many tributaries. In the High Moulouya valley, the right-side tributaries arisen from the High Atlas are: Oudrhès, Ansegmir, Outat, Adeghoual, Mibladen, Bousselloum, Bou-Adil; the left-side tributaries arisen from the Middle Atlas are: Kiss, Aguercif, Boulajoul, Sidi Ayad e Amrhid.

Most of them, with very low or absent flow for several months, are intermittent and flow occasionally only after long and protract rainfalls in torrential regime because of the presence of impervious rocks and the lack of vegetation (Ngadi, 1995). In the High Moulouya the droughts occur between May and January (mainly in July and August); the floods occur in

spring, mainly March and April for the Atlas Mountains snowmelt, and autumn, mainly September and October, following storms (El Hachimi, 2006).

Like all semi-arid regions with contrasting climatic seasons, Morocco periodically faces a rainfall deficit caused by recurrent droughts. In order to better manage these shortages, over the last decades a large-scale program for the construction of dams has been carried out to provide drinking water, irrigation and hydroelectric power (Direction de la Recherche et de la Planification de l'Eau, 1994). However, these reservoirs have suffered from siltation due to the hinterlands high rate of natural and accelerated erosion. According to Lahlou (1996), the annual sedimentation rate in Moroccan reservoirs reached 50 million m^3/year. This huge siltation has a serious environmental and socio-economical impact, since it reduces the reservoirs capacity, and could affect the morphological equilibrium of the coastline (Snoussi et al., 2002).

The transport of solid material after floods was very relevant for Moulouya River: the average was 12 g/l and the dams collection rate around 10 Mm^3/year (D.R.H.M., 1996). The annual average of Moulouya solid flows, mainly originated from Zeïda-Mibladen-Aouli abandoned mines, varied from 2000 ton/year in the upstream station (Zeïda) to 80000 ton/year in the downstream station (Melgeloidane): Moulouya river and some its tributaries (Mibladen, Adeghoual, Bousselloum, Bou-Adil, Sidi Ayad) drain those abandoned mines in the High Moulouya, stream in the Middle and Low Moulouya and flow toward the Mediterranean sea (Bendahou, 1995).

Since April 2001, the construction of the Sidi Saïd dam (capacity: 40 Mm^3) was carried out from the Moroccan kingdom in the High Moulouya valley, 20 km downstream of Zeïda mine; this dam, opened in April 2008, controls a water volume of 100 Mm^3 from Moulouya river (D.G.H., 2001). The dam mainly allowed to: a) manage the shortages; b) supply the request of irrigation water from Low Moulouya (around 717 Mm^3/year); c) defend downstream district (Middle and Low Moulouya) from floods; d) preserve the Mohammed V dam (Middle Moulouya) from overflows.

3.1.2 Groundwater

The High Moulouya hydrogeological basin is characterized by four main aquifer layers (Derrar, 1996):

1. the deep layer of Lias limestones which gives rise to some important sources (1 m^3/s);
2. the layer of Cretaceous limestones which gives rise to several little sources (600 l/s), for irrigation and watering;

3. the layer of Miocene conglomerates, used by more than 400 wells;
4. the layer of quaternaries alluvial sediments.

The general lack of current and accurate hydrogeological data leaded to difficulties in the study of groundwater setting of the Zeïda-Mibladen-Aouli abandoned mines area: sometimes the aquifer is in the quaternaries alluvial sediments and is a shallow aquifer (10-12 m) connected to the floods of the Moulouya river, sometimes it is a basal flow draining faults and joints of the sandstones and granites (Zeïda) or dolomites and metamorphic schists (Aouli) filling deep excavations (Mibladen).

3.2 Material and methods

3.2.1 Sample collection

All data reported here refer to sampling campaigns undertaken in 2007 and 2009.

The sampling network was designed collecting surface water and groundwater samples in several points (20) in and outside the mining areas and along the Moulouya river stream; in Fig. 3.1 and Table 3.1, the location of the sampling sites is given.

In order to investigate the impact of the mine activity in the High Moulouya valley, the sampling campaigns were directed to collecting water samples from: i) Moulouya river and its tributaries in and outside the three mining areas; ii) private wells outside the mining areas used for watering and irrigation; iii) abandoned wells occurred in the exploitation and processing sites; iv) deep excavations filled with groundwater and surface water.

During the first campaign, November 2007, five samples were taken into the Moulouya river and its tributary Mibladen approximately 15 cm below the surface of the water. In detail:

- a small dam localized outside Zeïda city centre (5);
- an area included between Mibladen and Aouli mines (1 and 2);
- the processing area of Aouli mine (3);
- downstream the mining sites in an agricultural area of Ksabi city (4) (external to the map in Fig. 3.1).

The second campaign was carried out in March 2009 in order to collect surface water and groundwater samples of the Moulouya basin. Fifteen samples were collected; in particular:

- groundwater samples from Moulouya basin upstream the mining areas (15, 16) (external to the map in Fig. 3.1);
- surface sample from Moulouya river in a small village outside Zeïda mining area (6);

- groundwater samples from groundwater filling deep excavations in processing and exploitation sites of Zeïda (8- 11; 13, 14) and Mibladen (19);
- groundwater samples from private wells area used for irrigation and watering in Zeïda (12, 17) and in Midelt area (20);
- surface water sample from the Sidi Saïd dam basin (7);
- groundwater sample from spring flowing from Aouli mine galleries (18).

Each sampling was carried out collecting water in three polyethylene bottles for the different analyses:

- SAMPLING A (1 L): for CO_2, HCO_3 content and ionic composition analyses;
- SAMPLING B (25 mL): for PTMs analysis;
- SAMPLING C (100 mL): for Fe and Mn content analysis.

In order to analyze metals content, polyethylene bottles for samplings B and C were previously acidified by nitric acid: respectively, ultra-pure HNO_3 (0.5 mL) and HNO_3 (2 mL).
A total of twenty samples of surface water and groundwater were collected in the two sampling campaigns; all sampling points were georeferenced by GPS in WGS84 geographical coordinates (latitude; longitude).

3.2.2 Analytical procedures

Some water parameters were measured on site:

- TEMPERATURE

Water temperature was obtained using a specific thermometer which gives temperature values expressed as °C. Temperature of water affects the solubility and hence the mobilization of chemical elements. At near neutral pH, solubility of chemical elements from their solid hosts generally increases with higher temperature.

- pH

The pH was measured using a portable pH-meter. Some PTMs will be mobilized by acid conditions and others under basic conditions. The pH then affects an environment's heavy metals status. For example, elements such as Cu and Zn are essentially immobile under basic pH conditions whereas Mo is mobile.

- CONDUCTIVITY

Used method consisted in direct determination of electrical conductivity measured by portable EC-meter which gives conductivity values expressed as $\mu S\ cm^{-1}$.
Other analyses were carried out in the laboratory of Dr. Trifuoggi (Chemistry Department – University Federico II of Napoli). All the samples were analyzed for CO_2, major ions (Na^+,

K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, NO_2^-, NH_4^+) , Fe and Mn content and PTMs total content.

- CO_2 CONTENT

CO_2 content in water samples (200 mL) was obtained by titration with NaOH 0.1223 M (indicator: phenolphthalein).

- HCO_3^- CONTENT

Bicarbonates content in water samples (100 mL) was obtained by titration with HCl 0.1029 M (indicator: bromocresol green).

- ANIONS AND CATIONS CONTENT

Anions and cations were determined by ion chromatography HPLC. The anions detected were: F^-, Br^-, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-. For cationic composition determination, the water samples were previously acidified (pH=3) by nitric acid (0.5 M); the anions detected were: Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+. The ions concentration was expressed as mg L^{-1}.

- IRON AND MANGANESE CONTENT

Water samples were previously acidified and filtered; Fe and Mn concentration was determined by atomic absorption spectroscopy and expressed as mg L^{-1}.

- PTMs TOTAL CONTENT

PTMs total content was determined by ICP-MS spectrophotometer. PTMs analyzed were: Al, As, Ba, Be, B, Br, Cd, Co, Cr, Cs, Cu, Fe, Hg, I, Mn, Mo, Ni, Pb, Rb, Se, Si, Sr, Ti, Th, U, V, W, Zn, Zr. The results were expressed as mg L^{-1}.

Table 3.1. Location of studied water samples

N°	Sample code	Mine	Altitude	Latitude	Longitude
				N	W
	Surface waters				
1	MR1	Mibladen	1164	32° 48' 79"	4° 36' 92"
2	MR2	Mibladen	1141	32° 48' 58"	4° 35' 73"
3	MR3	Aouli	1139	32° 48' 86"	4° 34' 91"
4	MR4	outside mining areas	1039	32° 50' 12"	4° 24' 32"
5	MR5	Zeïda	1462	32° 49' 03"	4° 57' 55"
6	MR6	Zeïda	1478	32° 47' 14"	4° 57' 56"
7	MR7	outside mining areas	1397	32° 47' 05"	4° 46' 13"
	Groundwaters				
8	gw1	Zeïda	1477	32° 47' 09"	4° 57' 36"
9	gw2	Zeïda	1478	32° 46' 38"	4° 57' 53"
10	gw3	Zeïda	1482	32° 46' 41"	4° 57' 58"
11	gw4	Zeïda	1443	32° 46' 58"	4° 57' 50"
12	gw5	Zeïda	1467	32° 49' 40"	4° 57' 29"
13	gw6	Zeïda	1466	32° 47' 31"	4° 58' 20"
14	gw7	Zeïda	1452	32° 50' 05"	4° 57' 11"
15	gw8	outside mining areas	1761	32° 56' 03"	5° 03' 19"
16	gw9	outside mining areas	2141	33° 01' 44"	5° 04' 15"
17	gw10	Zeïda	1602	32° 53' 54"	5° 00' 49"
18	gw11	Aouli	1140	32° 48' 39"	4° 35' 35"
19	gw12	Mibladen	1329	32° 46' 31"	4° 36' 53"
20	gw13	outside mining areas	1576	32° 38' 42"	4° 46' 04"

3.3 Results and discussion

3.3.1 Chemical characterization

Physical and chemical parameters and concentrations of dissolved components are reported in Table 3.2.

According to the literature (Hachimi et al., 2006), all waters were alkaline (pH: 7.2-9.4) due to the leaching from the mining areas.

Conductivity in groundwater was much higher (average: 2392 µS cm^{-1}) than that measured in surface waters (799 µS cm^{-1}) especially because of two samples from the processing area of Zeïda: 13 (15000 µS cm^{-1}) and 14 (5380 µS cm^{-1}).

As evidenced by the Piper diagram (Fig. 3.2), the majority of the waters were in *calcium-magnesium-bicarbonat*e facies. Only few samples moved away from this behaviour: in detail,

samples 1, 12 and 19 were in *calcium-sulphate* facies; samples 13 and 14 were in *sodium-chloride* facies.

The ionic composition of the water samples is also displayed using the Schoeller-Berkaloff diagrams (Fig. 3.3). Most of the studied waters were in *calcium-magnesium-bicarbonat*e facies with a Mg/Ca molar ratio close to 1 (Fig. 3.4); in two samples (6, 11) lower concentrations of the alkaline ions were detected. The Mg/Ca molar ratio increased in the spring water samples collected upstream of the mining areas (15, 16, 17) which were characterized by outcrop of dolomite rocks; however, a rilevant analytical error occurred in the samples 15 and 17. Also groundwater samples 18 and 19, which were collected downstream the mining areas in a dolostone plateau, exhibited high concentration of Mn, but the bicarbonate ion was substituted by the sulphate ion.

Samples 13 and 14 were in *sodium-chloride* facies with very high values of conductivity; possibly, these samples are not groundwater flowing towards lower piezometric levels but they are stagnant and represent brackish inland water bodies with very high salinity.

The difference between these waters and brackish waters is in the high content of HCO_3, which is the major anion in all the samples.

A significant content of SO_4 occurred in Mibladen in samples 1 (579 mg L^{-1}) and 19 (1007 mg L^{-1}); the highest content of NO_3 occurred in sample 12 (124 mg L^{-1}).

Also for the anionic composition the samples 13 and 14 were very different from the other groundwater samples: in particular, they displayed a much greater content of Cl (respectively, 2470 and 952 mg L^{-1}).

The content of Na and Cl was strictly correlated (r: 0.958; p-level: 0.000); the Na versus Cl plot in Fig. 3.5 shows that the most surface samples are aligned along a trendline which does not follow the seawater Na/Cl ratio line.

3.3.2 PTMs total content

Main PTMs total content in all water samples is reported in Table 3.3.

According to other results from the literature (Bouabdli, 2005), the main metallic contaminants in the studied area are Pb and Zn which in several samples are associated to high values of Cu, As and Cd.

The spring water samples collected upstream of the mining areas (15, 16, 17) were essentially uncontaminated.

Figure 3.6 shows the correlation graphs Zn/SO_4 (a) and Pb/SO_4 (b). All samples were characterized by low content of dissolved Zn average value in surface water samples (30.5 µg

L^{-1}) was higher than that in groundwater samples (7.7 µg L^{-1}). That depends on the solubility of zinc in water, which is a function of pH and total inorganic carbon concentrations; the solubility of basic zinc carbonate decreases with increase in pH and concentrations of carbonate species (WHO, 2008).

Most contaminated samples were collected in Mibladen (1 and 2) where Zn showed the highest values (respectively, 60 µg L^{-1} and 80 µg L^{-1}) and Pb values were 0.010 mg L^{-1} and 0.030 mg L^{-1}.

Several samples were contaminated by high values of Pb. Taking into account that the normal content of Pb in the natural waters is < 1-3 µg L^{-1} (Bowen, 1979; Hem, 1985), with the exception of samples 7, 16 and 20, all samples were characterized by higher values of Pb. Comparing the total content of Pb with the limit defined by the WHO (2008) for the drinking water (10 µg L^{-1}), only seven samples taken from Zeïda (6, 9, 11 and 12) and Mibladen (1, 2, 19) exceeded that limit (Fig. 3.7a). Moreover, Moroccan legislation allows a limit content of 50 µg L^{-1} for Pb in the waters: only the groundwater sample 19, collected from a deep excavation lake outcropping a Pb vein in Mibladen site (see Fig. 3.1), exceeded that limit.

With the exception of two samples (13 and 14), the concentration of As was always lower than the limit suggested by WHO (2008) for the drinking water (10 µg L^{-1}) (Fig. 3.7a); on the contrary, in almost all samples, the content of As exceeded the limit of 0.45 µg L^{-1} indicated by Casiot (1999) for fresh water.

A high content of Al and Fe was found in samples 6 and 11 from Zeïda area; as indicated by the Schoeller-Berkaloff chart (Fig. 3.3), the ionic composition of these samples was very similar. A contamination of Al was also detected in outcropping groundwater samples (14) collected in the mine tailings store of Zeïda (Fig. 3.7b). The amount of Fe was still high in the surface water samples 2, 4 and 5.

Fluoride in most samples was < 0.77 mg L^{-1}. The surface water sample with higher amount of F was sample 1, collected in Mibladen area (1.16 mg L^{-1}); the only samples with very high values of F were from the processing area of Zeïda (13: 6.97 mg L^{-1}; 14: 2.39 mg L^{-1}), where several cases of dental fluorosis occur in the population.

With regard to other elements, a high content of Ni was found in the sample 6 (0.028 mg L^{-1}) collected from Moulouya river in Zeïda area; groundwater sample 13 showed also a high content of B (1.4 mg L^{-1}). In all samples, dissolved Ba content ranged from 20 to 250 µg L^{-1} (average: 110 µg L^{-1}).

Table 3.2. Physical and chemical parameters and concentrations of dissolved components in surface and groundwater samples

Sample	T	Cond	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	NO_3	*error*	F	Br	NO_2	NH_4	Li
	°C	*µS cm^{-1}*		*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*		*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*
1	10.0	1401	8.3	82.54	11.44	165.04	80.66	92.46	579.04	163.24	16.80	*-3.14*	1.16	0.00	0.00	0.00	0.04
2	10.0	585	8.2	27.31	4.98	77.93	27.07	40.84	87.49	263.70	16.18	*0.85*	0.55	0.00	0.00	0.00	0.01
3	10.0	690	8.6	34.79	4.21	82.07	35.65	53.81	88.42	301.37	19.72	*-0.18*	0.66	0.00	0.00	0.00	0.02
4	9.0	849	8.2	43.70	3.78	103.50	46.22	60.98	175.36	313.93	12.57	*-1.12*	0.67	13.67	0.00	0.00	0.03
5	9.0	952	7.7	97.84	11.59	65.94	33.39	98.26	107.09	364.16	0.00	*1.77*	0.66	0.00	0.00	19.96	0.11
6	15.4	630	8.3	7.40	1.63	68.79	23.29	10.38	39.06	262.37	15.71	*-0.45*	0.08	0.00	0.00	0.00	0.04
7	15.1	486	8.6	12.81	2.33	53.56	18.96	12.39	32.62	213.56	8.40	*-1.94*	0.08	0.00	0.00	0.00	0.02
8	17.3	401	9.2	9.66	3.04	32.22	13.64	10.30	26.30	140.34	5.73	*0.05*	0.20	7.44	0.00	0.00	0.02
9	17.3	506	8.6	13.57	3.79	44.12	14.42	16.64	32.95	164.75	9.94	*-0.72*	0.22	0.06	0.00	0.00	0.03
10	18.0	773	8.5	31.62	3.40	42.69	29.36	33.24	58.65	219.66	5.83	*-1.30*	0.77	0.05	0.00	0.00	0.10
11	19.5	713	8.3	7.59	1.51	80.02	22.96	10.93	38.10	268.47	14.98	*-4.22*	0.03	0.10	0.00	0.00	0.02
12	18.5	2330	7.2	85.45	5.09	132.19	148.59	155.12	419.90	335.59	124.32	*-4.71*	0.48	0.46	0.00	0.00	0.07
13	20.5	15000	9.1	3430.82	78.55	9.50	136.15	2469.50	1244.35	3612.19	4.01	*-2.53*	6.97	4.22	0.00	0.00	6.22
14	18.0	5380	9.3	1267.26	23.88	15.70	52.63	951.46	1146.71	683.39	0.13	*0.88*	2.39	1.24	2.76	0.00	1.32
15	15.6	772	7.4	28.93	1.04	62.76	40.35	35.50	21.97	439.32	5.43	*6.14*	0.07	0.00	0.04	0.00	0.01
16	17.7	448	9.4	17.32	0.59	27.11	30.35	25.71	13.32	213.56	0.87	*-1.10*	0.05	0.00	0.00	0.00	0.01
17	15.2	990	7.6	39.78	0.04	56.51	58.55	77.48	25.16	475.93	24.04	*7.38*	0.13	0.21	0.00	0.00	0.02
18	17.6	748	8.4	23.43	6.80	38.27	48.50	42.41	57.52	292.88	1.24	*0.86*	0.33	0.18	0.00	0.00	0.09
19	15.1	2420	8.3	88.45	21.06	171.84	183.28	98.68	1007.08	244.07	18.04	*0.02*	0.63	0.37	0.00	0.00	0.11
20	13.5	612	7.6	21.61	1.70	79.00	22.06	44.79	23.58	244.07	27.43	*-4.19*	0.23	0.30	0.00	0.00	0.02

Table 3.3. Main PTMs total content in water samples

Sample	Al	As	Ba	B	Cd	Cr	Fe	Mn	Hg	Ni	Pb	Cu	Se	Si	Sr	U	Zn
	mg L^{-1}	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*µg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*µg L^{-1}*	*µg L^{-1}*	*µg L^{-1}*
1	-	< 0,001	0,06	0,15	< 0,0003	< 0,002	1	< 0,005	< 0,0005	< 0,001	0,010	< 0,010	< 0,001	4,5	2300	5,5	60,0
2	-	0,001	0,25	< 0,10	< 0,0003	< 0,002	3000	0,150	< 0,0005	< 0,001	0,030	< 0,010	< 0,001	13,0	1400	2,5	80,0
3	-	0,001	0,12	0,11	< 0,0003	< 0,002	150	0,020	< 0,0005	< 0,001	0,005	< 0,010	< 0,001	4,0	1800	3,0	8,0
4	-	0,001	0,12	0,11	< 0,0003	< 0,002	500	0,050	< 0,0005	< 0,001	0,006	< 0,010	< 0,001	5,5	2100	3,8	10,0
5	-	0,003	0,10	0,15	< 0,0003	< 0,002	250	0,150	< 0,0005	< 0,001	0,004	< 0,010	< 0,001	6,2	1200	15,0	40,0
6	11,25	0,002	0,15	< 0,10	< 0,0003	0,027	17332	0,472	< 0,0002	0,028	0,015	0,015	< 0,001	28,9	956	< 1,0	14,0
7	0,15	0,001	0,14	< 0,10	< 0,0003	< 0,001	88	0,018	< 0,0002	< 0,001	0,002	< 0,001	0,001	3,3	910	1,1	1,8
8	0,05	0,003	0,07	< 0,10	< 0,0003	< 0,001	24	0,029	< 0,0002	< 0,001	0,026	< 0,001	< 0,001	3,0	637	2,0	10,0
9	0,16	0,002	0,12	< 0,10	< 0,0003	< 0,001	97	0,036	< 0,0002	< 0,001	0,012	0,002	< 0,001	2,9	730	2,0	13,0
10	0,09	0,004	0,09	0,10	< 0,0003	< 0,001	50	0,018	< 0,0002	< 0,001	0,005	< 0,001	0,001	3,7	2475	8,0	< 1,0
11	2,59	0,002	0,10	< 0,10	< 0,0003	0,005	2511	0,190	< 0,0002	0,006	0,010	0,003	0,001	10,0	616	< 1,0	14,0
12	0,04	0,002	0,04	0,10	< 0,0003	0,001	28	0,004	< 0,0002	< 0,001	0,028	< 0,001	0,005	12,0	1782	7,0	< 1,0
13	0,15	0,096	0,07	1,40	< 0,0003	0,003	33	0,027	< 0,0002	< 0,001	0,007	0,040	0,007	7,2	2935	20,0	< 1,0
14	0,30	0,018	0,07	0,60	< 0,0003	0,003	130	0,025	< 0,0002	< 0,001	0,002	0,039	0,001	4,6	2699	14,0	< 1,0
15	< 0,02	< 0,001	0,03	0,10	< 0,0003	< 0,001	< 20	0,003	< 0,0002	< 0,001	0,004	0,014	< 0,001	3,9	138	< 1,0	5,3
16	0,05	< 0,001	0,02	< 0,10	< 0,0003	< 0,001	44	0,010	< 0,0002	< 0,001	0,002	0,004	0,001	0,3	96	< 1,0	8,5
17	< 0,02	< 0,001	0,24	< 0,10	< 0,0003	< 0,001	< 20	0,002	< 0,0002	< 0,001	0,003	< 0,001	0,002	9,4	405	< 1,0	< 1,0
18	< 0,02	0,004	0,06	< 0,10	< 0,0003	< 0,001	< 20	< 0,001	< 0,0002	< 0,001	0,006	0,002	0,002	6,4	1145	3,6	< 1,0
19	0,07	0,002	0,17	0,40	< 0,0003	< 0,001	64	0,028	< 0,0002	0,013	0,078	< 0,001	0,018	4,0	4358	8,2	7,7
20	0,02	< 0,001	0,08	< 0,10	< 0,0003	< 0,001	< 20	0,003	< 0,0002	< 0,001	0,002	< 0,001	0,002	6,0	1594	1,3	34,0

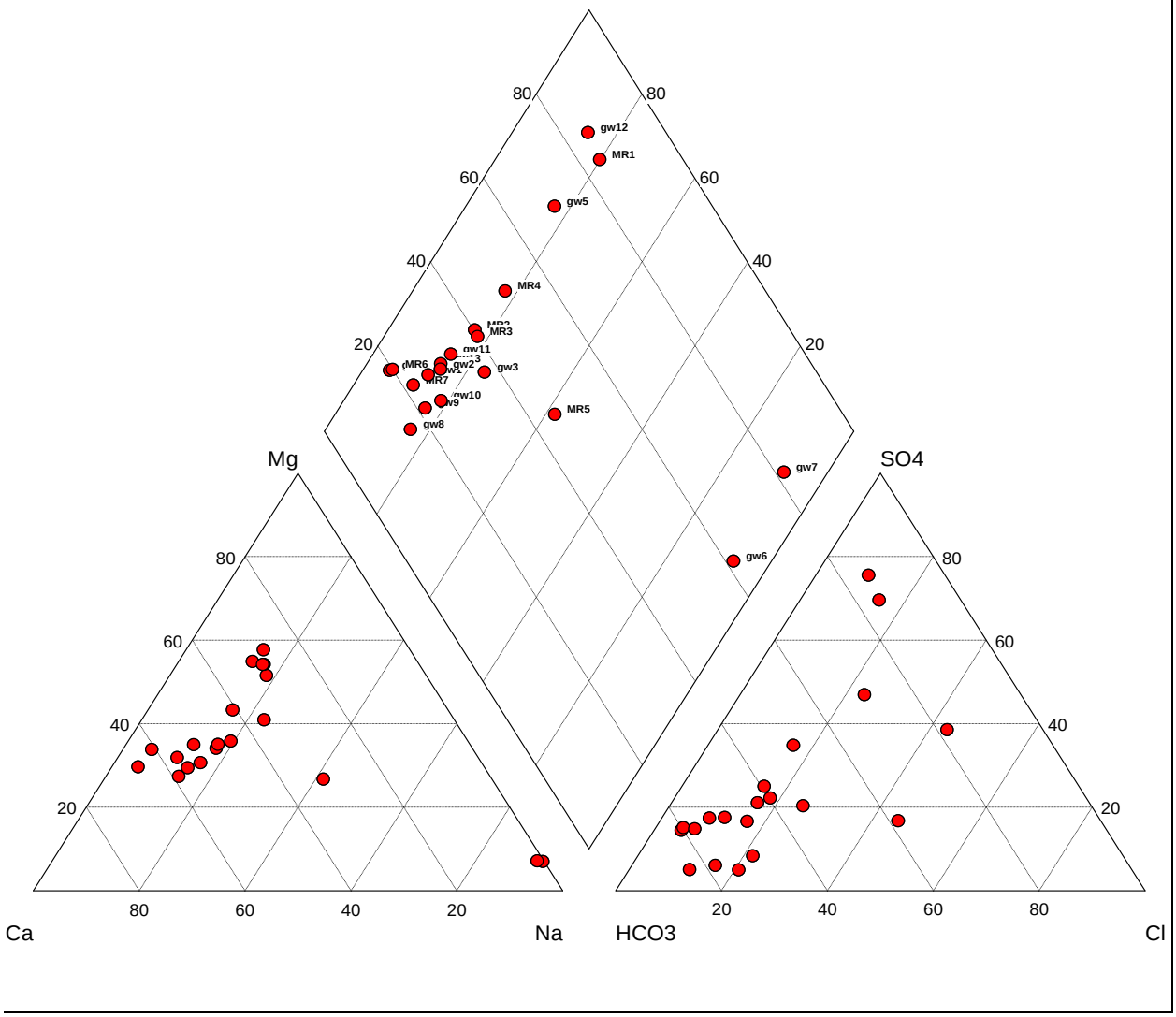

Figure 3.2. Piper diagram of the water samples (sample codes are in Table 3.1).

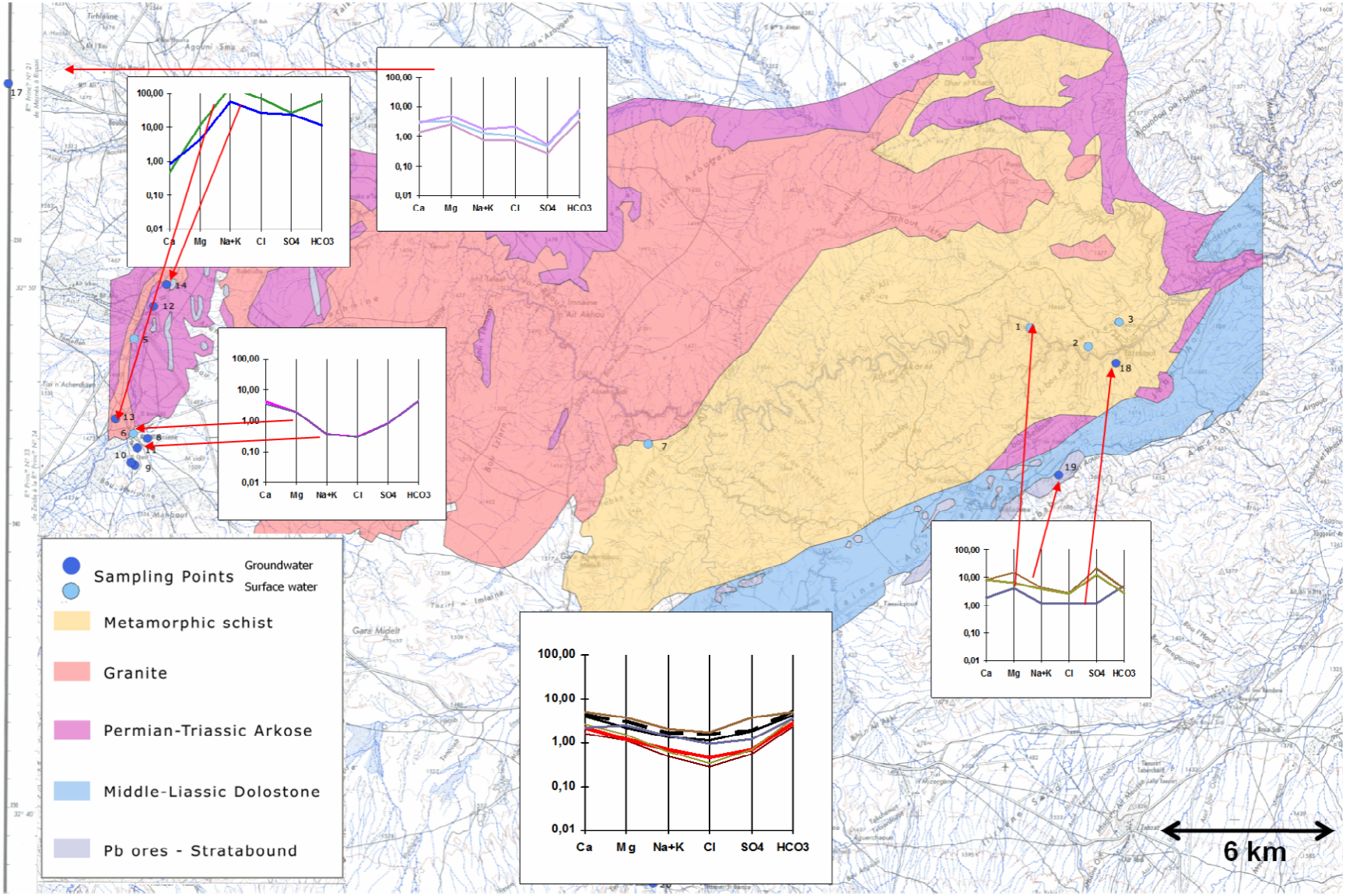

Figure 3.3. Shoeller-Berkaloff diagrams of the water samples.

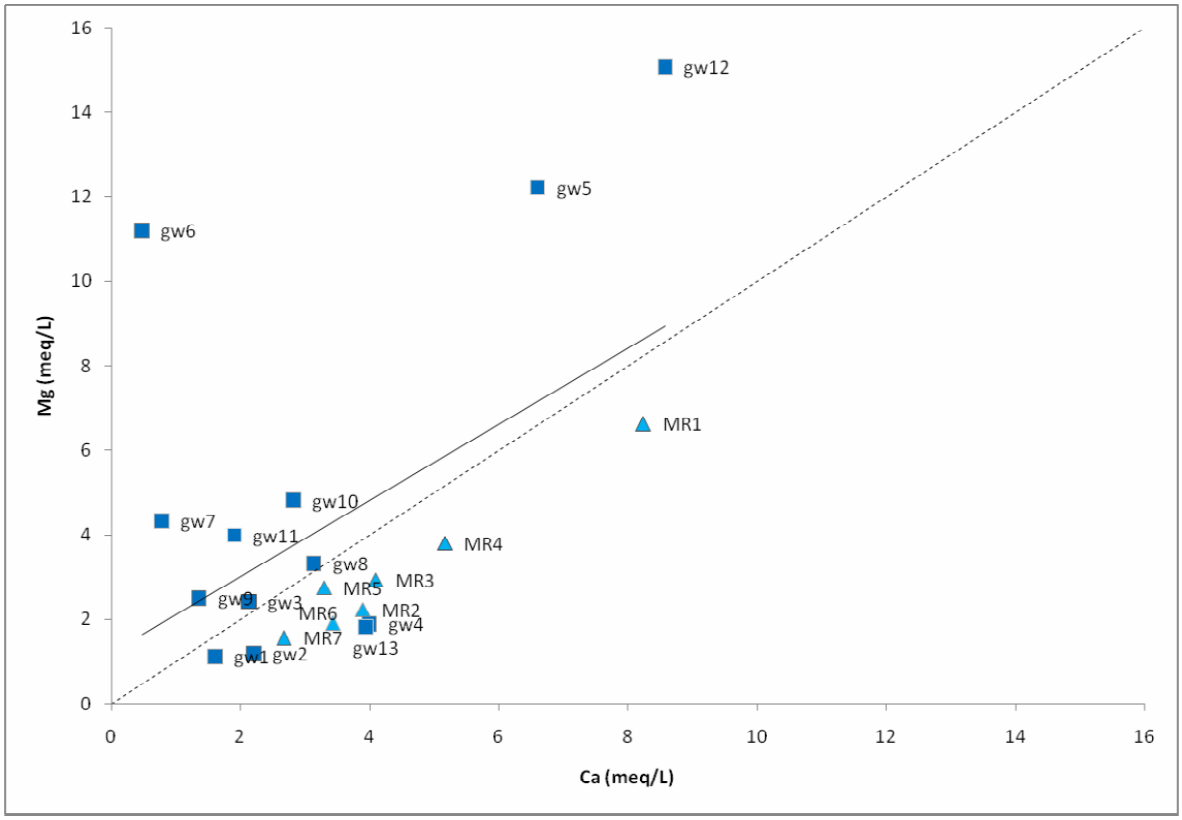

Figure 3.4. Dissolved Mg versus Ca concentrations in the waters; dotted line shows the Mg/Ca molar ratio equal to 1 (sample codes are in Table 3.1).

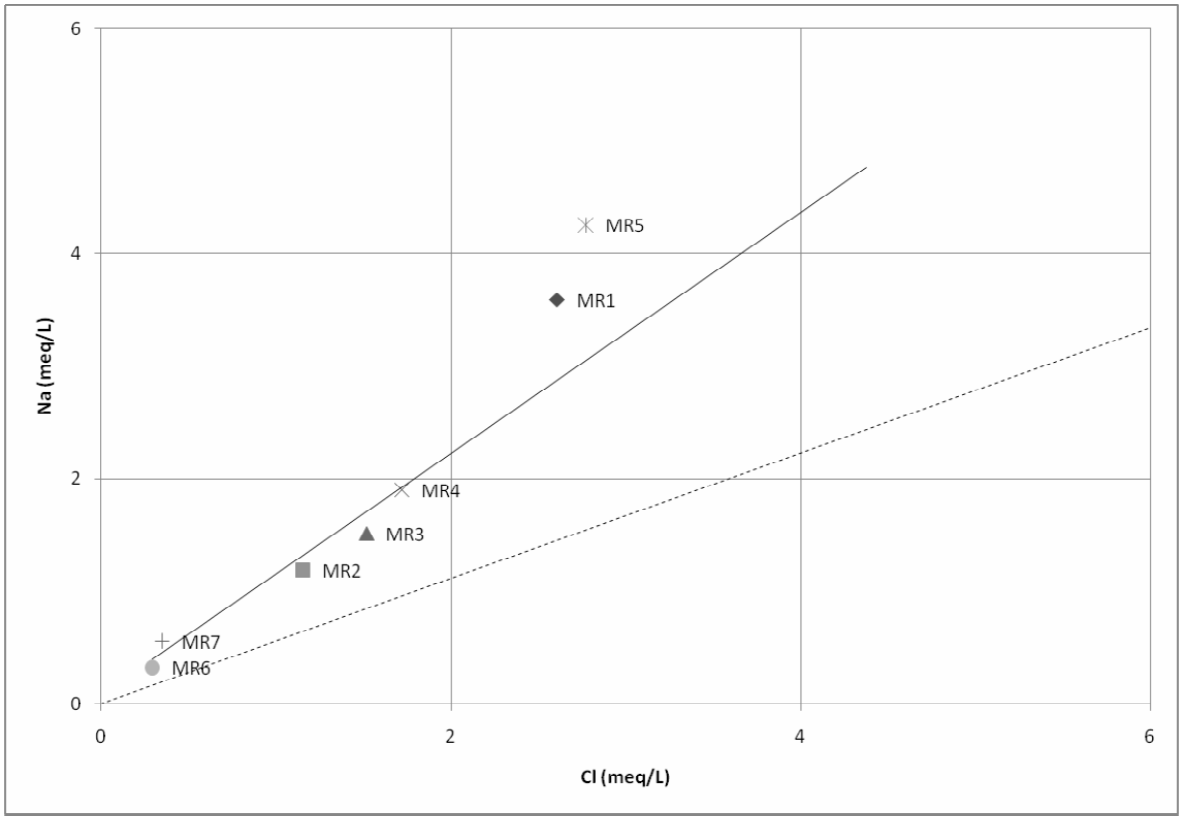

Figure 3.5. Dissolved Na versus Cl concentrations in the surface waters; dotted line shows the Na/Cl molar ratio in seawater (sample codes are in Table 3.1).

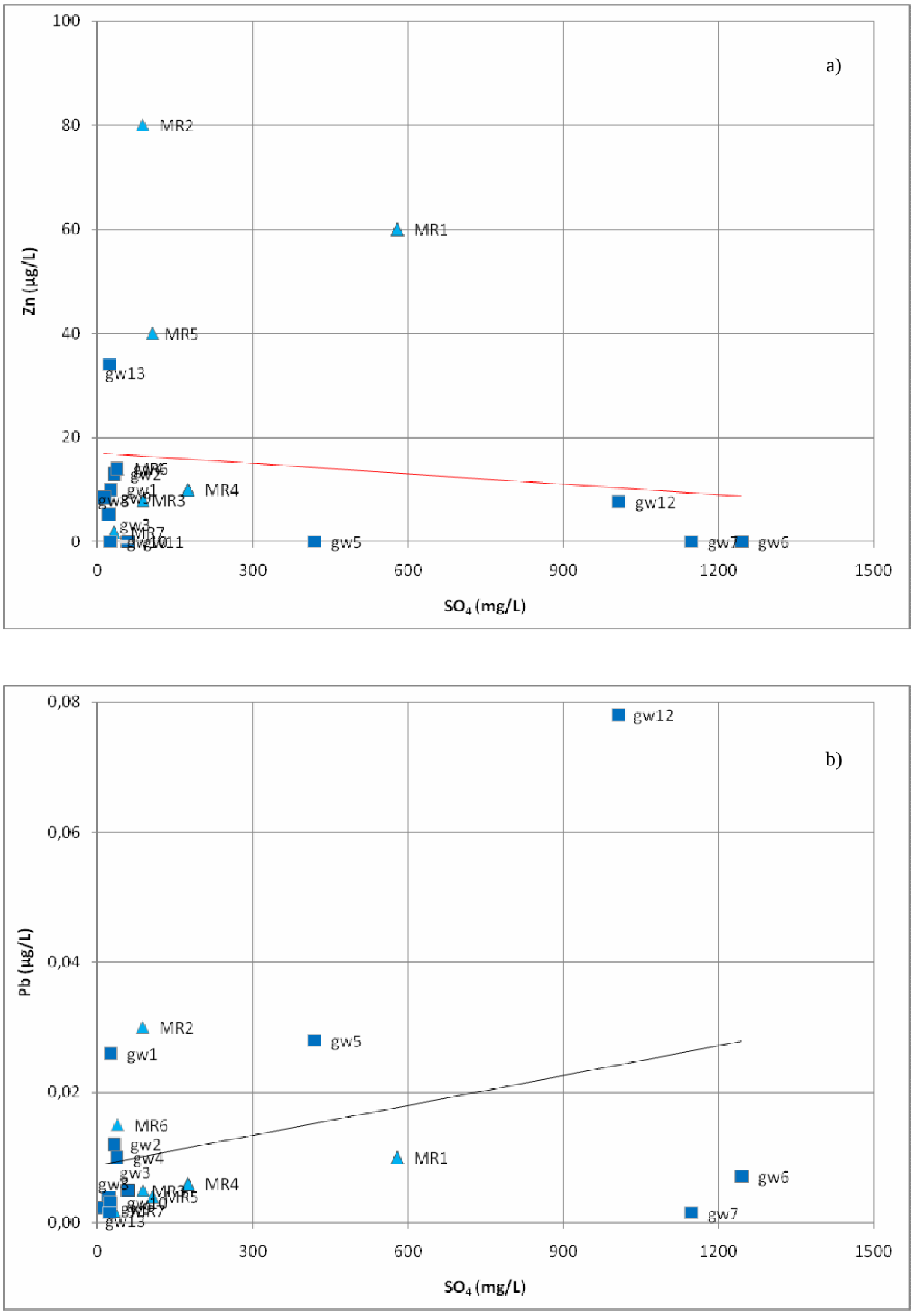

Figure 3.6. Dissolved Zn (a) and Pb (b) versus SO_4 concentrations in the water samples (sample codes are in Table 3.1).

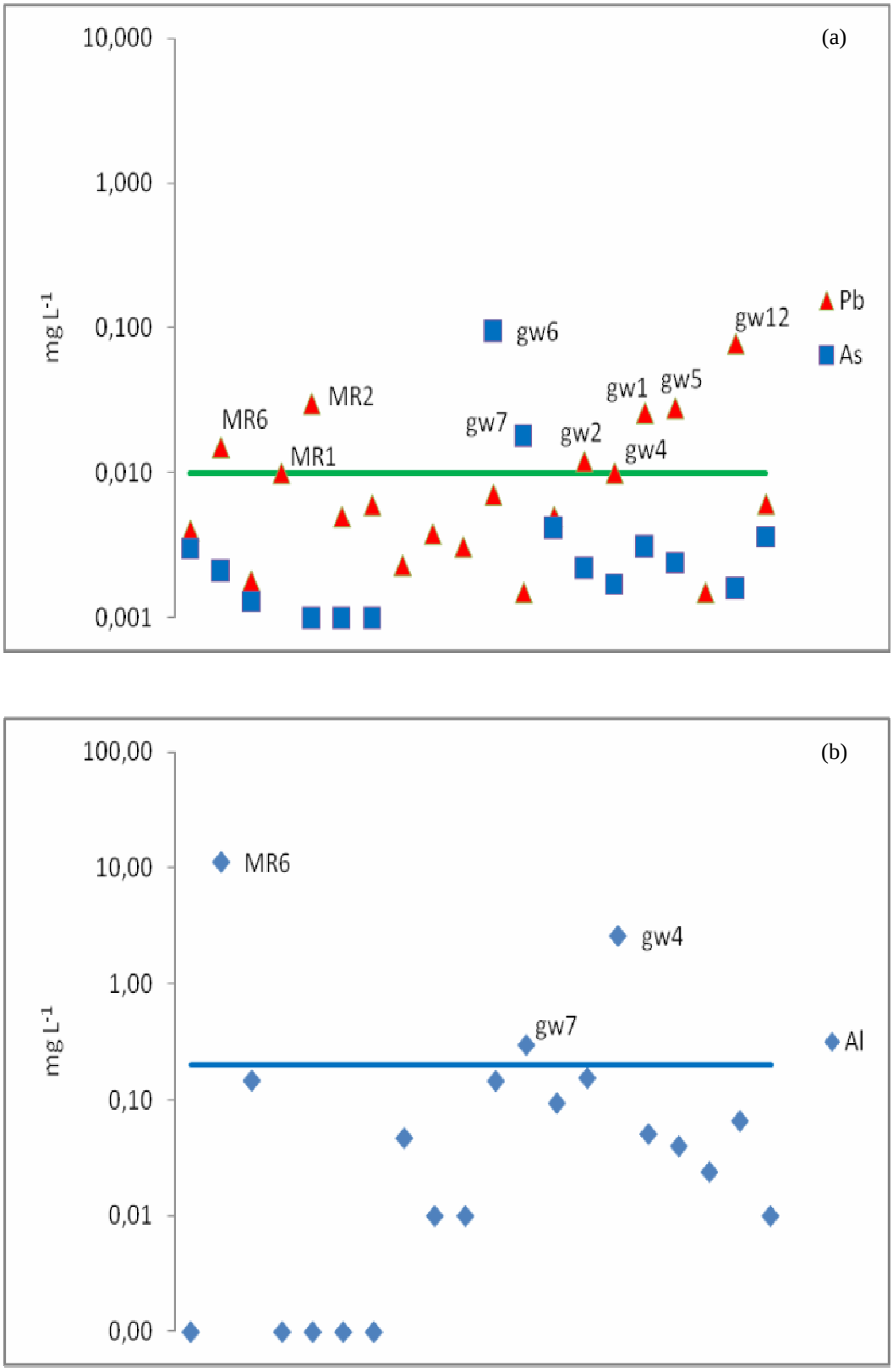

Figure 3.7. Concentration of Pb and As (a) and Al (b), in the water samples (sample codes are in Table 3.1); the line shows the limits for the drinking water (WHO, 2008).

3.4 Conclusions

The water chemical facies depends strictly on the embanking type of rock. Almost all waters are in *calcium-magnesium-bicarbonat*e facies. Moreover, surface waters and groundwater are characterised by very high pH values and high levels of HCO_3 in all the samples due to the leaching from the mining areas.

Generally, the amount of metals occurring in the water is low. The main contaminants occurring in some samples are prevalently Pb, As and Al.

The highest concentrations, especially of Pb, are recorded in the water samples collected downstream from the mines of Zeïda and Aouli.

The high levels of Zn recorded in soil profiles are not detected in groundwater because the solubility of zinc in water decreases with increase in pH and concentrations of carbonate species, both very high in groundwater. The higher values of Zn in surface waters depend on the transfer occurring by particles water and wind erosion.

Anyway, the contamination is restricted in the mining sites: surface water and groundwater samples collected outside do not show any evidence of contamination.

CHAPTER 4

CHEMICAL AND MINERALOGICAL SPECIATION OF LEAD AND ZINC IN SOILS AND MINE WASTES

4.1 Introduction

One of the common aims of studies that deal with soils or sediments contaminated with PTMs is to assess the fate and potential mobility of the contaminants, with respect to the environmental conditions that pertain to them now or in the future (e.g. Houba et al., 1996). For such purposes it is essential to determine the physical and chemical forms in which the metals reside, i.e. their speciation, not just the amounts of the various metals present (Ure and Davidson, 1995; Morin et al., 1999). From the perspective of risk assessment the following example illustrates the importance of speciation. Using total metal concentration as the index of risk it follows that a site with a concentration of 5000 mg kg^{-1} of Pb is significantly more toxic than one which is 500 mg kg^{-1} of Pb. However, suppose that the only species of Pb in the first soil was galena (lead sulfide, PbS; $K_{sp} = 10^{-27.5}$), while the only species of Pb in the second one was cerussite (lead carbonate, $PbCO_3$; $K_{sp} = 10^{-13.0}$). In absolute terms, from simple thermodynamic calculations alone, a greater amount of Pb is likely to be both mobile under water transport and bioavailable in soluble form to organisms in the soil with the lower Pb concentration, because cerussite is vastly more soluble than galena. Mobility is clearly dependent on chemical form. And although bioavailability and toxicity are complex processes and are biological species dependent as well as even genetically dependent within species, this example indicates that the chemical form of a metal contaminant is an important factor in assessing human health or ecological risks (D'Amore et al., 2005).

Most commonly the problem has been approached using either chemical or direct instrumental methods. Chemical methods seem to be the most popular, probably because they can readily provide a quantitative result. Chemical characterization includes not only the determination of total content of pollutants but also an estimation of chemical state which are bounded to wastes (easily exchangeable ions, metal carbonates, oxides, sulphides, organometallic compounds), which determine their mobility and pollution (Weisz et al., 2000; Yu et al., 2001). Typically, chemical methods are applied in various sequential extraction schemes (e.g. Li et al., 1995). Sequential extractions introduced by Tessier et al. (1979), based

on the use of selective phase-dissolving extractants, have allowed to identify the pools of elements of varying solubilities and mobilities (Renella et al., 2004). To simplify and harmonize the several existing procedures and improve the determination of extractable contents of trace metals in soil prior to certification, the European Community Bureau of Reference (Ure et al., 1993) established a four-step sequential extraction scheme based on the use of 0.11M acetic acid as first extractant.

However, it is now widely recognized that the forms determined by sequential extractions are inevitably operationally defined. As a consequence of such problems, instrumental methods such as X-ray diffraction, among many others, are often used to elaborate on the data obtained by chemical extraction schemes (e.g. Schön, 1995; Hudson-Edwards et al., 1996). X-ray powder diffraction (XRPD) is amongst the most versatile and useful of any instrumental technique for the identification of crystalline phases. Many aspects of clay mineral identification, such as interstratification of two or more types, are not readily accessible by any other technique (Hillier, 2003). The study of clay minerals is always most fruitful when a range of complementary techniques is utilized (Wilson, 1987). Nonetheless, XRPD is undoubtedly one of the most powerful techniques for the analysis of clay minerals.

In addition to identification XRPD can also be used to make quantitative analyses of the amount of any phase present in a mixture (Zevin and Kimmel, 1995; Jenkins and Snyder, 1996). Many different procedures can be used to obtain quantitative information from XRPD data but they have traditionally required a considerable investment of time compared to the relatively straightforward use of XRPD for phase identification (Hillier et al., 2001) based on searching and matching reference XRPD patterns to those of unknown materials. Quantitative analysis by XRPD is a more difficult undertaking, especially when the samples contain complex mixtures of phases, as is often the case with samples from contaminated sites or from waste materials (Winburn et al., 2000; Hillier et al., 2001). Despite their limits to define and quantify the mineralogical associations when metals are present in very small amounts (Essington and Mattigod 1991), these methods appeared pertinent when coupled with chemical and physical approaches to provide a better understanding of contamination history and to improve assessment of environmental risks and remediation feasibility (Hillier et al., 2003). Therefore, even though both sequential extraction and direct methods have severe limitations, a combination of the two approaches may provide a more realistic picture of the actual forms of PTMs in soils.

In this Chapter heavy metal speciation by sequential chemical extractions and quantitative mineralogical determination by XRPD were applied to define Pb and Zn chemical and

mineralogical forms and phases in the mine wastes and soils from the former lead mining district of the High Moulouya valley (Morocco). The aim was to provide base line data required to assess metal mobility and transferability.

4.2. Materials and Methods

4.2.1 Chemical speciation

The fractionation of Pb and Zn among geochemical phases was carried out on the fine earth of selected samples: the mine wastes from all three mining areas (ZT, MT, MC1, AT), surface soil samples from the exploitation areas of Zeïda and Mibladen (ZP1, MP1), surface and deep soil samples from the processing area of Mibladen (MP2, MP3) and surface soil sample collected outside Mibladen site (SS). In Fig. 2.1 and Table 4.1, the location of these sampling sites are given.

The four-step sequential extraction procedure developed by the Measurement and Testing Program of the European Commission (Ure et al., 1993) was modified according to Renella et al. (2004) in order to differentiate the carbonate bound fraction (Table 4.2) by introducing a preliminary step based on the shaking of soils with 1M NH_4NO_3 buffered at pH7 which is suitable for measuring available metals in sequential extractions (Krishnamurti et al., 2000). Acetic acid has been considered unsuitable for studying PTM speciation in calcareous soils because it gives poorly reproducible results (Carlton-Smith and Davis, 1983) and dissolves carbonates and makes it difficult to discriminate between the adsorbed and carbonate fractions; even if dilute acetic acid does not dissolve well crystallized carbonates such as calcite and aragonite (Ray et al., 1957) it could dissolve the highly reactive fine carbonate present.

In this work the sequential extraction procedure consisted of five steps; the metal phases which are presumed to be sequentially extracted are:

1. Sample (1 g) was placed in 100-ml volume Teflon bottles with 40 mL of 1M NH_4NO_3 shaken for 2 hours, and then the mixture was centrifuged at 3000 rpm for 20 minutes. The extract was stored at 4 °C until analysis; the residue was washed with 20 ml of deionized water and centrifuged at 3000 rpm for 20 minutes. This fraction (*labile pool*) is the most labile pool bonded to the wastes, and therefore, the most dangerous and bio-available for the environment. It consists of exchangeable and soluble metals in calcareous soil.

2. Forty mL of 0.11M acetic acid (pH=2.5) was added to the residue and the mixture was shaken for 16 h at room temperature. The extract was separated from the solid residue by centrifugation (3000 rpm for 20 minutes), decanted into a polyethylene bottle and stored at 4 °C until analysis. The residue was washed with deionized water (by centrifugation at 3000 rpm for 20 minutes) and the washings discarded. This fraction (*HOAc-extractable*) corresponds to carbonate-bound metals.

3. Forty mL of 0.1M hydroxylamine hydrochloride (adjusted to pH of around 2 by adding HNO_3) was added to the residue in the same centrifuge tube. Again, the extraction was performed as described in 2nd step. This fraction (*reducible*) represents Pb and Zn bound to Fe and Mn oxides that can be released if conditions change from oxic to anoxic state.

4. Ten mL of 8.8M H_2O_2 (pH 2.0–3.0) was added carefully in small aliquots into the residue. The tubes were covered and the contents digested for 1 h at room temperature and 1 h at 85 °C in a water bath. Then, volume was reduced to around 2–3 ml by further heating the uncovered tube. This step was performed twice (e.g., more details in Sahuquillo et al., 1999). At the end of the oxidation the H_2O_2 was allowed to evaporate completely. After cooling, 50 mL of 1.0M ammonium acetate (adjusted to pH 2 by adding HNO_3) was added to the residue, which was extracted as described in 2nd step. This fraction (*oxidizable*) is made up of metals bound to sulphides and organic matter, which may be released under oxidizing conditions.

5. Soil residues were transferred to the microwave reaction bombs for complete mineralization. The residue was digested adding 16 mL of aqua regia (a mixture of 12M HCl and 15.8M HNO_3 in the ratio 3:1), 4 mL of HF and 6 mL of H_3BO_3. The extract was separated from the solid residue by filtering, decanted into a polyethylene bottle and stored at 4 °C until analysis. This residual fraction (*residual*) includes Pb and Zn tightly associated with crystalline oxides and in the mineral lattice structure which are therefore unlikely to be released from the mining wastes.

It is important to emphasize that these metal phases are nominal target only, operationally defined by the extraction used. The concentration of Pb and Zn in the various extracts was determined by a Perkin Elmer AAnalyst 700 spectrometer; the efficacy of the extraction procedure and the analytical quality of the AA data were controlled by including one sample of a BCR Standard Reference Material (BCR701 – lake sediment) of known composition in each analytical batch of samples.

Table 4.1. Location of selected soil and mine waste samples

N°	Sample code	Site	Latitude	Longitude
			N	W
	Mine Z (Zeïda)			
1	ZP1	Expl.	32° 48' 26"	4° 58' 17"
4	ZT	Proc.	32° 50' 24"	4° 57' 05"
	Mine M (Mibladen)			
10	MP1	Expl.	32° 45' 16"	4° 39' 02"
12	MP2	Proc.	32° 45' 42"	4° 38' 41"
13	MP3	Proc.	32° 45' 53"	4° 38' 41"
14	MT	Proc.	32° 45' 44"	4° 38' 40"
15	MC1	Proc.	32° 45' 39"	4° 38' 43"
16	SS	out	32° 40' 57"	4° 37' 27"
	Mine A (Aouli)			
24	AT	Proc.	32° 48' 40"	4° 35' 34"

P = soil profile; T = tailing; C = coarse waste rock; SS = surface soil;
Expl. = exploitation area; Proc.: processing area; out = outside mining area

Table 4.2. Sequential extraction procedure for the fractionation of PTMs

STEP	Extractant	Presumed metal forms
1	1 M NH_4NO_3	Soluble and exchangeable (labile pool)
2	0.11M HOAc	Carbonates bound (HOAc-extractable)
3	0.5 M NH_2OH HCl	Occluded in ‘easily reducible’ Mn and Fe oxides (reducible)
4	1M H_2O_2 / NH_4OAc	Organic matter associated and sulphides (oxidizable)
5	HCl / HNO_3 / HF 3:1:1	Mainly in primary minerals lattice structure (residual)

4.2.2 Mineralogical analysis

Mineralogical analysis was undertaken on the fine earth of all solid samples and on selected clay fractions. For X-ray powder diffraction (XRPD) all samples were prepared by two different procedures. The first procedure involved the spray-drying sample preparation and the quantitative determination of phases; the second procedure involved only hand grinding of the dry samples in an agate mortar and pestle and was made essentially to check that the wet milling and spray drying procedure had not resulted in any noticeable phase changes.

Spray drying is a samples preparation method capable of producing truly random powder samples for X-ray powder diffraction (XRPD). Essentially samples are prepared as an aqueous slurry and sprayed through the airbrush into a heated chamber; in the chamber the spherical spray droplets dry forming spherical granules. Both the spherical shape of the granules and the way spheres pack together in a powder holder ensures random arrangement of the component particles. In addition, indeed as a consequence of eliminating preferred orientation, the XRPD pattern of spray dried samples are extremely reproducible (Hillier, 1999). Sample preparation is a crucial step and if the properties of the slurry are not suitable the process is likely to fail: the slurry needs to have as high a content of solids as possible in order to minimise drying time and to ensure that the droplets retain a spherical shape as they dry; moreover, the slurry must still be dilute enough to be sprayed easily through the airbrush at low pressures without clogging it up. The solid samples (3 g) were placed in a McCrone micronising mill together with an appropriate amount of ethanol and the mixture was milled for 12 min to reduce the particle size to normally less than 10 µm. Ethanol was chosen as the slurry liquid rather than water to allow spray-drying at a lower temperature in case the samples contained temperature sensitive phases such as sulfates. The resulting slurries were spray dried directly from the mill at a temperature of 60 ºC (Hillier, 1999).

The resulting powder samples were top loaded into 2.5 cm diameter circular cavity holders and XRPD patterns recorded on a Siemens D5000 with a θ/θ goniometer and Co Kα radiation, chosen with a diffracted beam monochromator. Diffraction patterns were obtained by step scanning from 2 to 75° 2θ, with a step size of 0.02°.

Additionally, in order to aid identification of the clay minerals present in the samples, the < 2 µm size fractions were also prepared as oriented mounts using the filter peel method (Drever, 1973) and scanned in the air-dried state, after ethylene glycol solvation by vapor pressure overnight followed by heating at 300 ºC for 1 h. These scans were recorded from 2 to 45º 2θ in 0.02º steps.

Qualitative analysis was the first step used to identify the phases present in the samples and was accomplished using reference patterns from the International Center for Diffraction Data (ICDD) powder diffraction (1998) file and Bruker Diffract Plus EVA™ software, together with consideration of data from the < 2 µm clay fraction analysis.

Quantitative analysis was made only on the bulk spray-dried samples using two different approaches. At first, the Rietveld method of quantitative analysis was applied to the diffraction data using the commercially available software package Siroquant V3 (Taylor, 1991). Essentially, the Rietveld method involves fitting the observed diffraction pattern with a synthetic pattern which is a sum of patterns calculated for each phase in the sample from which the relative abundances are obtained.

A further quantitative analyses was carried out using full-pattern fitting in order to better evaluate the content of clay minerals. Standard reference patterns were prepared by spray-drying mineral phases as pure samples and as samples spiked with 50 wt.% corundum as an intensity reference. Where necessary, detectable impurities were subtracted electronically from the reference patterns and allowance was made for their concentration in the spiked standards when calculating full-pattern RIRs. The fullpattern fitting was done using an EXCEL™ spreadsheet and the SOLVER™ add-in to minimize an objective function dependent on the difference between the observed diffraction pattern and a pattern composed of a sum of single-phase reference patterns (Omotoso et al., 2006).

The spreadsheet-based method is essentially a variant of those implemented in FULLPAT (Chipera and Bish, 2002) and ROCKJOCK (Eberl, 2003) spreadsheets. In the first cycle of the fitting process, the proportions of the reference patterns were allowed to vary; in the second cycle, all patterns, including the unknown, were allowed to shift independently by a fraction of a step (±0.02º) along 2θ; in the third and final cycle the proportions were again allowed to vary. Shifts along 2θ were accommodated by a cubic spline function, as suggested for differential XRD by Schulze (1986). Several fitting runs were made for each sample. Reference minerals were obtained from the Macaulay Institute mineral collection and from private mineral collectors. Trace phases which had not been recognized initially were added and/or different reference patterns of the same phase were tried in attempts to improve the fit. For some phases, several reference patterns of the same phase were used simultaneously to aid in accounting for differences between the phases present in the samples and the standards.

4.2.3 X-Ray fluorescence spectrometry

In this study the determination of total metal content was carried out on the selected samples listed in Table 4.1 by X-ray fluorescence spectroscopy (XRF) in order to compare these concentrations to those obtained from the mineralogical analysis by fullpattern fitting method.

X-Ray fluorescence spectrometry was carried out under contract at GAU-Radioanalytical Laboratories, Southampton University, UK. Analysis was carried out using a Philips Magix-PRO XRFS, end-window 4kW rhodium target tube and SuperQ4 software. Calibration of the instrument was carried out using the Trail Lachance matrix correction. The flux used was ICPH Fluore-X 65 containing 66% lithium tetraborate and 34% lithium metaborate. Samples were prepared as pressed powder pellets by mixing the flux and the dried sample at a ratio of 10:1, with the addition of two drops of potassium iodide. The mixture was fused at 1150 °C for 10 min and cast into a Pt-5Au tray. Loss-on-ignition was carried out separately on a duplicate sample.

4.3 Results and discussion

4.3.1 Chemical speciation

The Pb and Zn fractions operationally defined by the sequential extraction are here in referred to as ‘labile pool’, ‘HOAc-extractable’, ‘reducible’, ‘oxidizable’ and ‘residual’, respectively. The distribution of Pb and Zn in the tailings and selected soil and mine waste samples within the operationally defined fractions is reported in Tables 4.3a and 4.3b. The relative amounts of Pb and Zn expressed as a per cent of the cumulative total extracted are given in Fig. 4.1.

For Pb a satisfactory agreement ($r = 0.991665$; $p < 0.001$) was found between the gross total obtained by a single determination (in Table 4.4b) and the cumulative total as extracted by the sequential extraction scheme (Table 4.3a). Thus the Pb cumulative total fell within -12% and +9% of the gross total in the majority of the samples, sometimes deviating by 26-55% and in SS sample by 361% (Fig. 4.2a).

For Zn the deviation between the cumulative and gross total amounts was larger than Pb. The Zn cumulative total fell within -35% and +21% of the gross total in the majority of the samples, deviating up to 578% in the others (Fig. 4.2b).

Samples inhomogeneity and differences in analytical methodologies can be taken into account to explain the deviations which were found. Soil samples contaminated by mining/industrial activities are known to be characterised by metal contaminants not uniformly distributed in all

soil volume, but strongly associated with specific soil solid phases (Davidson et al., 1998; 1999). Thus inhomogeneity can produce large deviations in the measured total values. Moreover, in this study total analysis was a single determination carried out by XRF, while chemical fractionation and therefore cumulative total determination was performed by acid digestion followed by ICP-MS. Finally, total and sequential extraction analyses are performed on different aliquots of the same sample, which are therefore not identical in chemical composition. In the majority of the studied soils and mine wastes, Pb was mostly concentrated in the HOAc-extractable and reducible fractions, although it was also present in other fractions (Table 4.3a). In the highly contaminated materials (tailings: ZT, MT, AT; soil: MP3; mine waste: MC1) from 53 to 82% of total Pb was associated with the HOAc-extractable fraction. In the case of ZP1, MP1 and MP2 soils, the reducible followed by the HOAc-extractable fraction contained most of the Pb (from 58 to 70%). In SS soil, the greatest percentage of Pb (66%) was present in the reducible fraction. In MP1 soil, the residual fraction (36%) also contained a significant portion of total Pb. The contribution of the labile fraction to total Pb was relatively low in all studied materials (from 0.00% in ZP1, MP1 and SS to 6.4% in ZT). Nevertheless, in some cases the concentration of the labile (soluble and exchangeable) forms are not negligible (ZT: 230 mg kg^{-1}; MP3 72-92 cm: 173 mg kg^{-1}; MC1: 218 mg kg^{-1}). Like Pb, most of the Zn in the studied soils and mine wastes was present in the HOAc-extractable (1-81%) and reducible (5-81%) fractions. The HOAc-extractable fraction tends to prevail in the most contaminated materials, which in the case of Zn are all from the Mibladen area. In the case of MP1 soil, containing the lowest total content of Zn (42 mg kg^{-1}), the greatest percentage of Zn (64%) was present in the residual fraction. In the less contaminated SS and ZP1, the reducible was the most important fraction (respectively, 51% and 81%), followed in SS by the organic one (40%). Only in MP2, the most Zn contaminated soil, the concentration of the labile forms of Zn were considerably high (489 mg kg^{-1}).

The sequential extraction used in this study is useful to indirectly assess the potential mobility and bioavailability of metal contaminants in soils and mine wastes. Assuming that bioavailability is related to increasing extractants strength and decreasing phases solubility, then metal bioavailability decreases in the order: labile > HOAc-extractable > reducible > oxudizable > residual fraction. Based on the results, the amount of Pb and Zn present in the residual fraction was low in all studied materials, with the exception of SS soil. On the contrary, a large percentage of the total Pb and Zn was in the no residual fractions, mainly associated with carbonate and Fe-Mn reducible oxides, with low contributions by organic and exchangeable forms.

Table 4.3a. Content (mg kg^{-1}) of lead in the sequentially extracted fractions and cumulative totals in the selected studied soil and mine waste samples

Sample code	Depth (cm)	Labile pool	HOAc-extractable	Reducible	Oxidizable	Residual	Cumulative total
Mine Z (Zeïda)							
ZP1	0-6	0	28	128	77	37	270
ZT	0-20	230	2149	1110	20	85	3594
Mine M (Mibladen)							
MP1	0-15	0	16	22	2	21	61
MP2	0-23	68	3936	5558	1743	2324	13629
MP3	0-35	52	5826	1185	452	669	8184
	35-45	44	11740	1300	1025	155	14264
	72-92	173	13503	1721	1521	287	17205
MT	0-20	61	8240	1007	808	329	10445
MC1	0-20	218	2618	715	506	71	4128
SS	0-10	0	2	172	49	39	262
Mine A (Aouli)							
AT	0-20	11	1772	1228	178	161	3350

Table 4.3b. Content (mg kg^{-1}) of zinc in the sequentially extracted fractions and cumulative totals in the selected studied soil and mine waste samples

Sample code	Depth (cm)	Labile pool	HOAc-extractable	Reducible	Oxidizable	Residual	Cumulative total
Mine Z (Zeïda)							
ZP1	0-6	1	3	243	53	0	300
ZT	0-20	3	94	327	20	39	483
Mine M (Mibladen)							
MP1	0-15	0	4	11	0	27	42
MP2	0-23	489	44477	80972	48474	14932	189344
MP3	0-35	63	1152	518	520	223	2476
	35-45	4	673	69	145	88	979
	72-92	3	409	56	88	0	556
MT	0-20	30	310	90	70	52	552
MC1	0-20	34	1772	108	264	0	2178
SS	0-10	0	2	120	93	18	233
Mine A (Aouli)							
AT	0-20	3	157	126	31	58	375

Table 4.4a. Oxides content of selected samples by XRF analysis

Sample code	Depth *(cm)*	SiO_2 *wt %*	TiO_2 *wt %*	Al_2O_3 *wt %*	Fe_2O_3 *wt %*	MnO *wt %*	MgO *wt %*	CaO *wt %*	K_2O *wt %*	Na_2O *wt %*	P_2O_5 *wt %*
Zeïda											
ZP1	0-6	48.9	0.6	9.2	4.6	0.9	3.3	16.3	3.1	0.2	0.14
	6-36	47.4	0.61	8.8	4.8	0.6	3.6	18.3	3.1	0.2	0.13
	36-52	45.8	0.65	10.1	5.0	0.5	4.2	17.9	3.4	0.2	0.1
ZT	0-20	72.8	0.15	10.1	0.7	0.0	0.6	1.9	5.9	0.8	0.04
Mibladen											
MP1	0-15	46.2	0.4	5.2	2.4	0.1	5.9	20.3	1.6	0.1	0.12
	15-45	49.3	0.5	7.0	3.0	0.1	6.1	17.1	2.0	0.1	0.13
	45-75	54.0	0.44	6.7	2.8	0.1	6.5	14.6	1.9	0.1	0.12
MP2	0-23	14.5	0.22	3.6	4.3	0.1	6.1	21.7	0.6	4.0	0.08
	23-50	19.2	0.3	4.7	4.1	0.2	11.0	23.0	0.8	2.6	0.08
	50-90	42.3	0.79	13.5	5.8	0.1	6.5	18.8	2.4	0.2	0.08
MP3	0-35	24.6	0.29	3.6	2.0	0.2	12.4	21.6	0.8	0.2	0.05
	35-45	21.5	0.36	5.2	2.4	0.3	13.6	22.5	0.8	0.2	0.04
	45-72	11.1	0.24	2.3	1.4	0.3	15.0	26.1	0.3	0.2	0.03
	72-92	35.0	0.55	9.4	3.5	0.3	11.7	19.4	1.6	0.3	0.06
	92-150	18.8	0.29	3.0	1.7	0.2	14.8	26.0	0.5	0.3	0.04
MT	0-20	16.4	0.25	3.0	1.5	0.2	14.3	23.1	0.6	0.2	0.03
MC1	0-20	22.3	0.36	5.1	2.4	0.4	17.0	28.4	0.9	0.1	0.04
SS	0-10	39.8	2.06	11.6	9.1	0.3	3.0	19.6	5.4	0.7	0.54
Aouli											
AT	0-20	30.8	0.49	6.1	3.2	0.2	8.4	22.8	1.6	0.4	0.07

Table 4.4b. PTMs total content of selected samples by XRF analysis

Sample code	Depth	Pb	Zn	Ni	V	Cr	As	Cu	Ba	Co	Rb	Sr	Y	Zr	Nb	U	S	Cl
	(cm)	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*mg kg^{-1}*	*%*	*%*
Zeïda																		
ZP1	0-6	174	124	690	101	276	34	44	1816	26	108	279	24	318	12	4	0.08	0.01
	6-36	168	125	771	82	392	33	44	1165	18	125	432	24	277	12	4	0.07	0.13
	36-52	156	102	592	89	272	28	52	1081	19	166	585	30	252	13	7	0.05	0.01
ZT	0-20	3484	664	2539	48	559	101	56	27532	1	229	1242	23	92	7	8	0.70	0.00
Mibladen																		
MP1	0-15	62	51	976	35	362	7	10	1461	10	35	279	15	212	8	2	1.34	0.02
	15-45	60	64	962	47	353	7	12	911	10	46	279	18	245	10	3	0.98	0.02
	45-75	41	56	992	38	359	6	10	655	7	45	226	17	221	8	2	0.74	0.02
MP2	0-23	12673	64291	1200	113	190	717	1200	5773	10	32	286	7	80	4	1	0.15	0.03
	23-50	11193	48728	630	153	169	540	818	21274	15	37	743	9	89	5	2	0.46	0.04
	50-90	355	2443	126	140	157	19	24	1910	2	72	217	19	171	12	3	0.07	0.02
MP3	0-35	6476	3796	637	421	254	213	379	134561	11	33	3461	8	41	3	2	2.84	0.03
	35-45	13037	287	223	424	155	405	139	138005	14	40	3490	7	48	4	2	2.69	0.03
	45-72	3127	281	204	527	141	122	102	192008	12	13	4457	2	17	3	0	3.83	0.02
	72-92	17253	167	278	257	175	457	134	53619	11	72	1523	13	111	8	3	1.21	0.04
	92-150	5659	148	426	368	196	184	86	127231	10	20	2979	7	79	5	1	2.69	0.05
MT	0-20	6230	1224	248	495	148	217	135	178875	15	27	4580	4	23	3	0	3.62	0.02
MC	0-20	7652	559	173	208	126	215	88	54762	15	37	1374	10	80	5	1	1.22	0.01
SS	0-10	57	193	607	485	457	20	35	2747	29	109	1194	38	523	153	7	0.08	0.01
Aouli																		
AT	0-20	2593	539	678	233	272	84	70	71220	11	51	2012	12	143	10	3	1.72	0.01

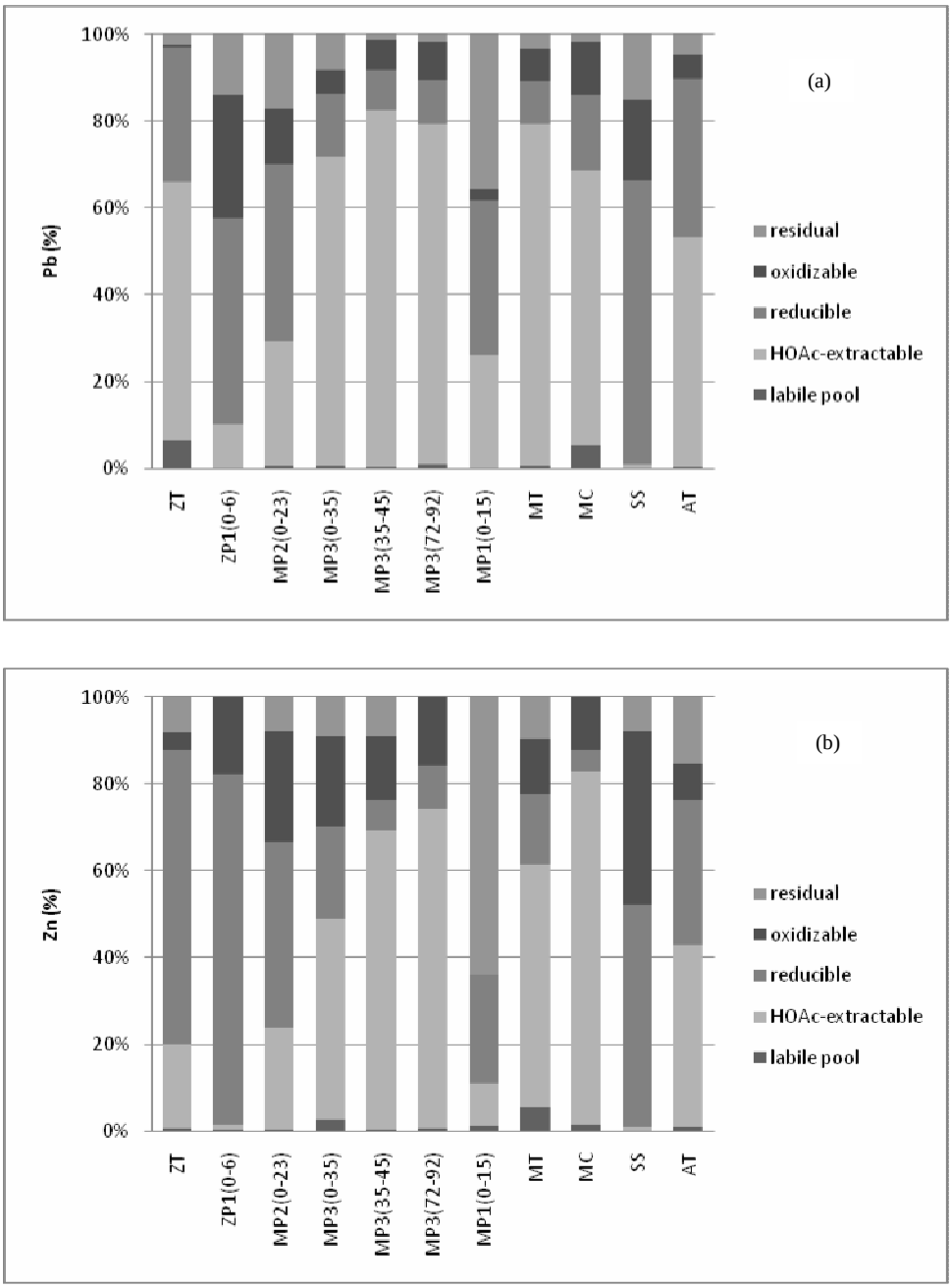

Figure 4.1. Percentage contribution of lead (a) and zinc (b) in the sequentially extracted fractions.

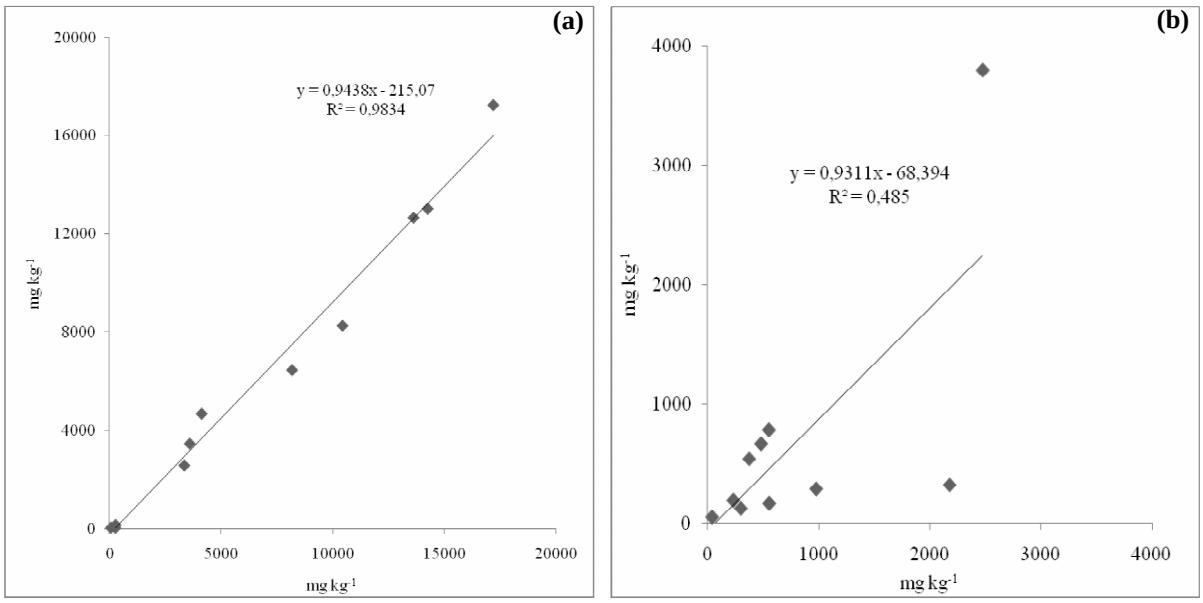

Figure 4.2. Relation between the gross total obtained by a single determination and the cumulative total as extracted by the sequential extraction scheme for Pb (a) and Zn (b).

4.3.2 Mineralogical analysis

The quantitative mineralogical analysis data reported in this Chapter refer only to results obtained by the fullpattern fitting method as they are more accurate in calculating the content of clay minerals in agreement with the qualitative analysis undertaken on the < 2 µm size fractions.

The main mineralogical phases detected in all samples from the High Moulouya mining district consisted of the carbonates, dolomite and calcite, along with quartz; the samples from the processing area of Mibladen were also rich in barite (Fig. 4.3).

In total, 27 crystalline mineral phases were positively identified in samples from the three mining sites investigated. Mineralogical group and name for these phases were: carbonates, calcite, cerussite, dolomite, hydrozincite, smithsonite; oxides, goethite [FeO(OH)], hematite [Fe_2O_3], magnetite [Fe_3O_4], quartz; sulphates, anglesite, barite, gypsum [$Ca(SO_4)2H_2O$]; sulphides, galena, sphalerite; fluorides, fluorite; K-feldspars, microcline [$KAlSi_3O_8$], orthoclase [$KAlSi_3O_8$], sanidine [$(K,Na)(Si,Al)_4O_8$]; plagioclases, albite [$NaAlSi_3O_8$], labradorite [$(Ca,Na)(Si,Al)_4O_8$]; pyroxene, augite [$(Ca,Mg,Fe^{2+},Fe^{3+},Ti,Al)_2(Si,Al)_2O_6$]; silicates, hemimorphite, willemite; clay minerals, chlorite [$(Fe,Mg,Al)_6(Si,Al_4)O_{10}(OH)_8$], illite [$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2(H_2O)$], kaolinite [$Al_2Si_2O_5(OH)_4$], montmorillonite [$(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$].

The soil profile from the Zeïda exploitation site (ZP1) was especially rich in calcite (average: 24%), quartz (38%) and clay minerals (23%). In the tailings ZT, the content of quartz was still very high (50%), but carbonates and clay minerals were almost absent and replaced by K-feldspars (30%).

The soil from Mibladen exploitation site (MP1) was characterized by a high content of quartz (average: 56%), dolomite (16%) and calcite (11%). Different was the proportion of the main mineralogical groups in the soil samples from the Mibladen processing area (MP2 and MP3), where the main mineral phases consisted of dolomite (average: 39%), quartz (16%) and barite (15%); also the Mibladen mine wastes (MC and MT) were prevalently made of dolomite (44%) and barite (22%). The composite surface soil sample taken outside the Mibladen area consisted mainly of K-feldspars (24%), calcite (24%) and diverse clay minerals (17%).

The main mineralogical phases in the tailings of Aouli were quartz (24%), dolomite (24%), clay minerals (15%) and calcite (15%).

Based on the detailed characterisation of the phases present in the samples, eight of all detected minerals have been shown to contain Pb and Zn in their structures: cerussite, anglesite, galena, hydrozincite, smithsonite, sphalerite, willemite and hemimorphite.

Cerussite has been found in the waste materials of all mines (ZT: 0.6%, MC: 0.4%, MT: 1.2%, AT: 0.3%) as well as in the soil profiles from the Mibladen processing area (average MP2: 0.9% and MP3: 1.0%); in this area little amounts of anglesite (MP2 50-90cm: 0.4%) and galena (MP3 35-45 cm: 0.4%; MP3 72-92 cm: 0.3%; MT: 0.1%) were also found.

Zinc minerals were detected only in soil and waste samples from the Mibladen processing area; in particular, in the first two horizons of MP2 soil (MP2 0-23 cm: willemite 8.2%, smithsonite 8.9%, hemimorphite 17.2%, hydrozincite 5.9%; MP2 23-50 cm: willemite 5.0%, smithsonite 9.1%, hemimorphite 9.3%, hydrozincite 5.4%) and in the tailings (MT: sphalerite 0.4%). The presence of willemite is rather peculiar, because this mineral is either derived from high temperature ore deposits (certainly not those of the High Moulouya district), or it is one of the products of Zn-ore smelting.

Concerning the vertical distribution of the mineral phases containing Pb and Zn, their content was found only in the soils from the processing area of Mibladen (MP2 and MP3).

Along the soil profile MP2 (Fig. 4.5), the percentage of mineral phases containing Pb and Zn showed a decreasing trend with depth as well as the content of Pb and Zn (see Fig. 2.9).

Also along the soil profile MP3 (Fig. 4.6), where Zn-rich minerals were not found, the content of Pb and the amount of Pb minerals showed the same behaviour with high and low values alternating down along the profile.

4.3.3 Comparison between chemical and mineralogical data

Using typical compositions for Pb and Zn in the mineral phases and the concentrations of each phase in the investigated samples, based on the fullpattern fitting XRPD analysis, it is a simple matter to calculate the concentrations of Pb and Zn present in the most contaminated samples for comparison with directly determined geochemical data as a validation of the quantitative mineralogical analysis. In figure 4.7, the results of these calculations are shown; clearly, the total concentrations obtained from the mineralogical analysis are comparable to those obtained by XRF. As an additional control to achieve better evaluation of chemical and mineralogical data, calculations were performed also for barium, an element that was also highly concentrated in the studied samples, especially in those from Mibladen processing area. However, Ba (in form of barite-$BaSO_4$) is considered almost immobile in the local weathering conditions, not causing any additional pollution.

The results obtained for Pb and Ba is encouraging since they give some confidence that the fullpattern fitting XRPD analysis has provided accurate quantitative mineralogical results.

Indeed, the total contents of Pb and Ba calculated through mineralogical data were very similar to those measured by XRF (for Pb, r = 0.9458; slope value = 0.911; y-intercept = 930 mg kg^{-1}; for Ba, r = 0.9773; slope value = 0.9488; y-intercept = 2204 mg kg^{-1}). For Zn, whose mineral occurrence was restricted to the Mibladen processing area, there was a consistent difference between the content calculated by the mineralogical identification and that measured by XRF. Mineralogical computation appears to overestimate Zn total content or XRF has underestimated it. This incongruence could also be explained taking into account the inhomogeneity of the samples which in the case of Zn is likely more pronounced than for Pb. The occurrence of Zn bearing mineral phases in the studied materials is limited to soils and wastes taken in the Mibladen processing area and is referable to the irregular discharge in this area of Zn-rich extraction residues. The irregular distribution of these Zn-rich materials in soils and waste dumps may have produced sample inhomogeneity. Moreover XRF and XRPD analyses were carried out on different aliquots of samples, which are not necessarily similar.

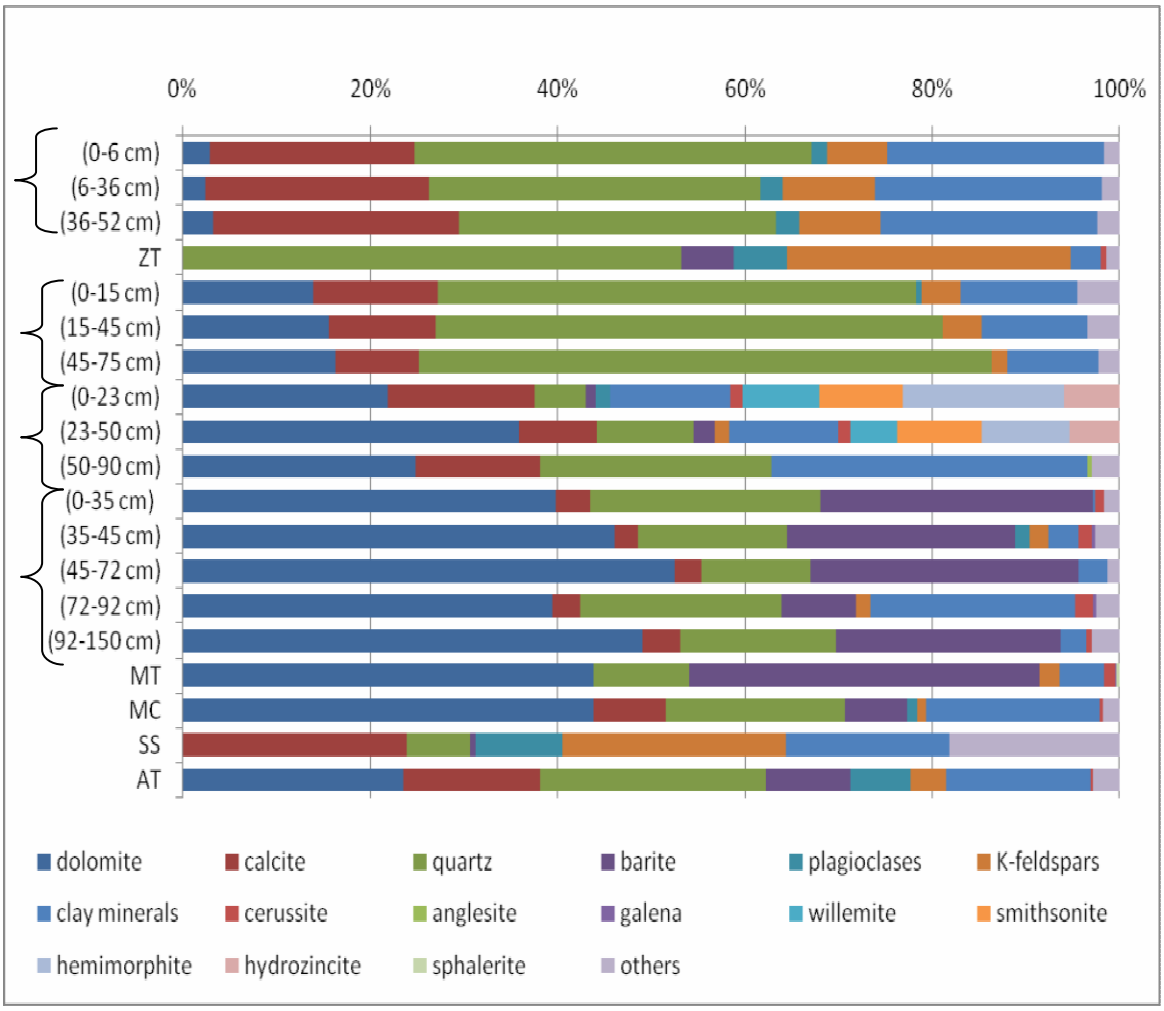

Figure 4.3. Mineralogical composition of studied soil and mine waste samples.

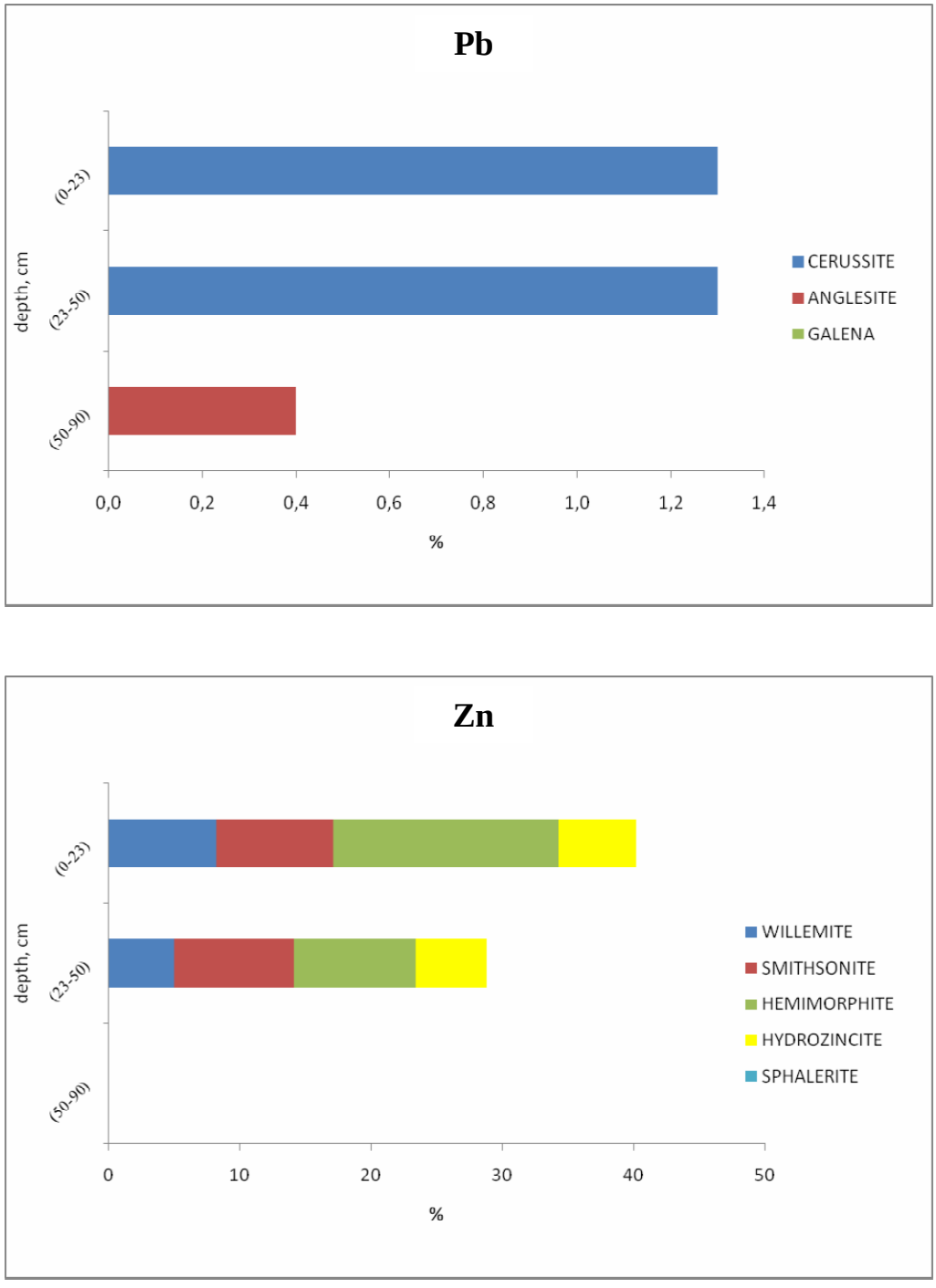

Figure 4.5. The vertical distribution of Pb and Zn mineral phases in the soil sample MP2.

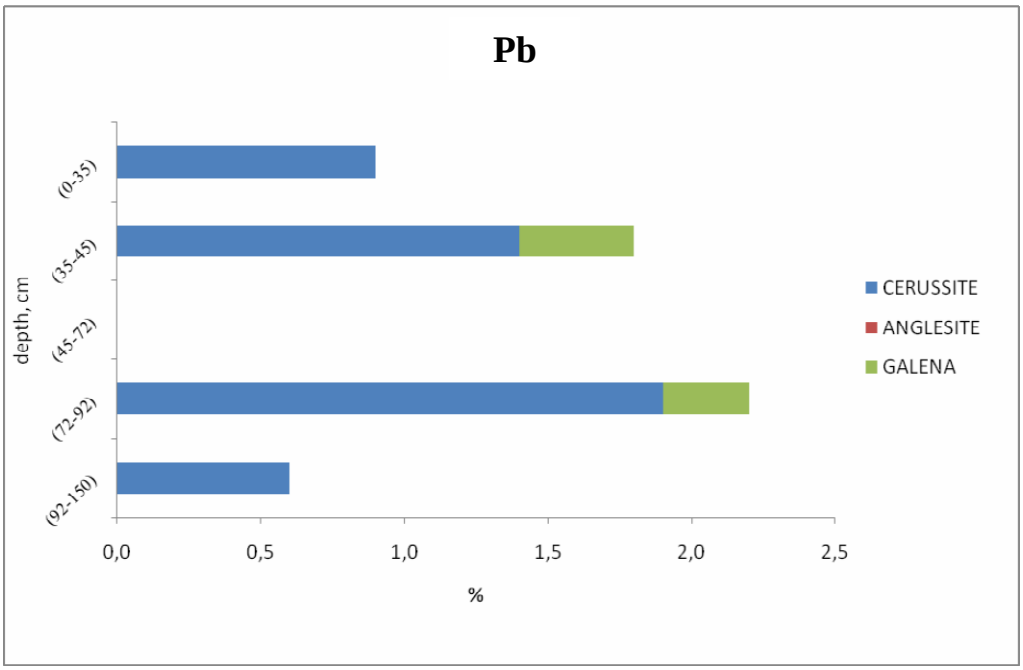

Figure 4.6. The vertical distribution of Pb mineral phases in the soil sample MP3.

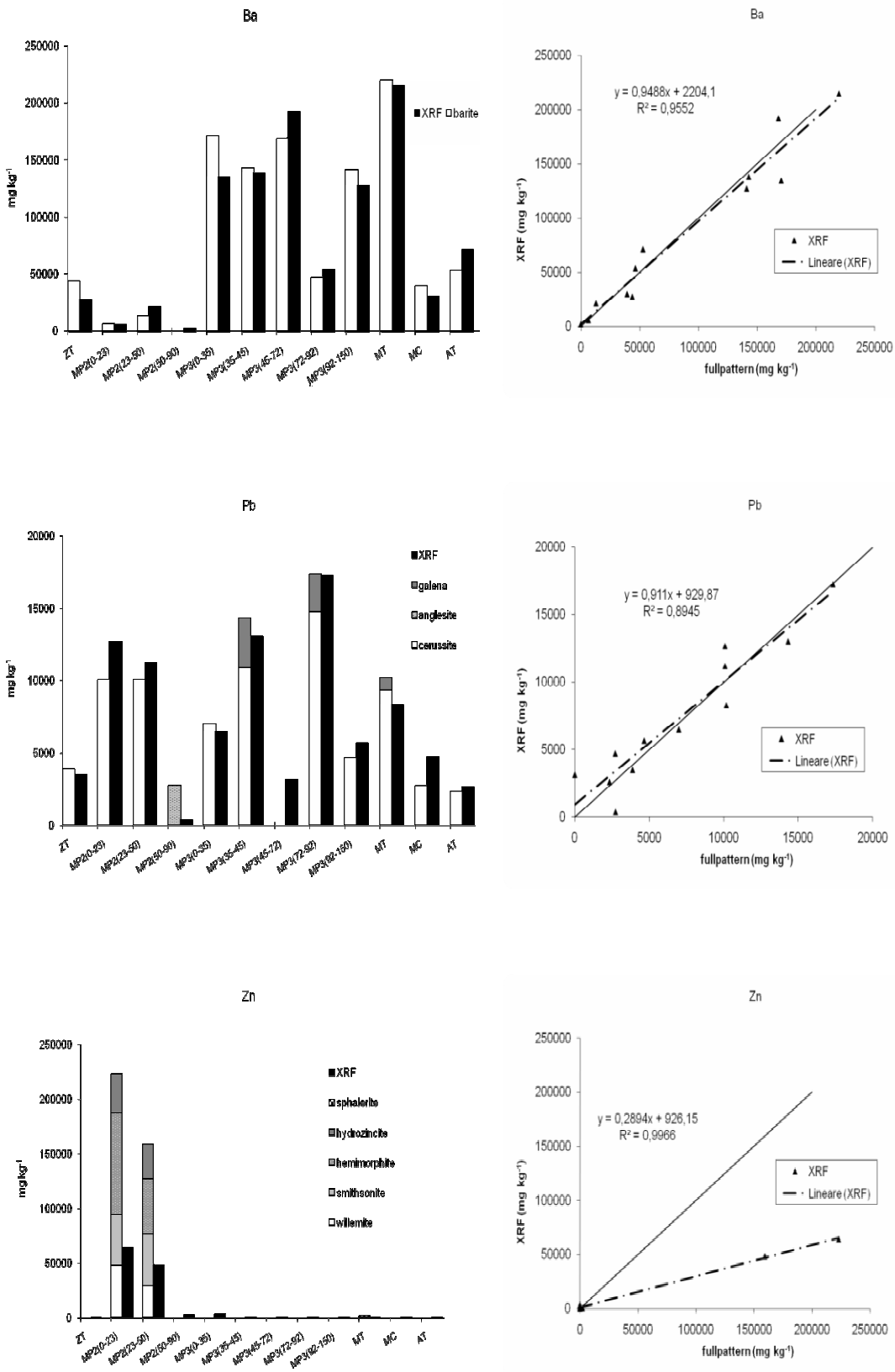

Figure 4.7. Comparison XRF-fullpattern: Ba, Pb and Zn concentrations in most contaminated samples.

4.4 Conclusions

The complexity of metal contaminated sites has and continues to be simplified to a measure of the total metal content. While total metal content is a critical measure in assessing risk of a contaminated site, total metal content alone does not provide predictive insights on the bioavailability and fate of the metal contaminants (D'Amore et al., 2005). Their mobility and the corresponding toxicity in the soil depends on their chemical concentration in the soil solution, the nature of their association with other soluble ionic species (chemical speciation), the soil's ability to release the elements from the solid phase (chemical speciation of soil solids) and the identification of crystalline forms present in the soil (mineralogical speciation) (Krishnamurti and Naidu, 2003).

Selected wastes and soils from the Upper Moulouya mining district were analyzed by sequential chemical extractions and XRPD fullpattern fitting method in order to assess the chemical and mineralogical forms of the main metal contaminants.

Based on the chemical speciation results, in the majority of the studied soils and mine wastes, Pb and Zn were mostly concentrated in the HOAc-extractable and reducible fractions.

In particular, the major association of Pb and Zn with the HOAc-extractable fraction in the highly contaminated soils and wastes is in agreement with the occurrence in these materials of Pb and Zn carbonates (see mineralogical results); when the content of these mineral phases drops down in the less or not contaminated soils and wastes, Pb and Zn become prevalently bound to Fe and Mn reducible oxides.

Mineralogical quantitative analysis of the investigated samples from the High Moulouya valley indicated that cerussite was the most important Pb-host in all mining and processing sites. The main Zn sources found only in Mibladen processing site were hemimorphite and smithsonite.

In relation to the minerals solubility, the mobility of Pb and Zn within the studied environment is limited: most likely the metals are displaced through physical transport of fine particles.

The low amount of heavy metals occurring in soluble forms in the soils inside and outside the mining areas as well as in the river water and sediments points to a negligible transfer of contaminants to the nearby environment. The low solubility of heavy metal main mineral phases and the presence of a high proportion of carbonates largely affect the transfer of the metals reducing their mobility from mine waste by dissolution; in the whole area the transfer can possibly occur only by wind and water erosion of the finest fractions.

CHAPTER 5

OVERALL CONCLUSIONS

Soil has long been regarded as a repository for society's wastes. Gradually mobilized by biogeochemical processes, soil contaminants can pollute water supplies and impact food chains. Heavy metals such as Cd, Cu, Pb and Zn are all potential soil pollutants. Their distribution among specific forms varies widely based on the metals chemical properties, on the forms in which metal reaches the soil and on soil characteristics.

It is therefore necessary to have guidelines for PTMs in soils which consider not only their total contents but also mobility, availability and toxicity of contaminants, in order to predict adverse effects and define appropriate strategies of remediation.

The Moulouya River is the largest river in Morocco; it rises in the Atlas Mountains and flows into the Mediterranean Sea. The upper zone of its basin is also known as the Upper Moulouya lead mining district because of the occurrence of three mining areas (Zeïda, Mibladen and Aouli) where mainly galena and less frequently barite and cerussite have been mined.

Since 1985 all three mines were closed: the abandoned mining and metallurgic equipment left on the surface together with all the accompanying waste materials, including tailings, have seriously modified the natural landscape of the High Moulouya valley and created an important source of contamination. The studied area is characterized by severe erosion problems caused by wind and water runoff in which soil and mine spoil texture, landscape topography and regional and microclimate play an important role: PTMs contained in the residues from mining operations can be dispersed by wind and/or water after their disposal.

On the basis of this investigation, the main contaminants of wastes, soils, sediments and waters collected in the High Moulouya valley are Pb and Zn often associated with V, Co, Cu, Cd, Sn, As and Sb. Zinc was not extracted in the studied area so the high levels of this element indicate that Zn-containing ores from other Moroccan mines were accumulated and processed in the High Moulouya district plants.

The risk associated to metal contamination is appreciable from the standpoint of potential mobility and bioavailability of Zn and Pb found in very high values in all wastes and in the materials sampled in the processing areas. In studied soils and wastes, availability of metal contaminants to plants and microbiota is affected by both alkaline pH and carbonate. The latter can be considered as source and sink of the metals, according with the presence of metal-bearing crystalline carbonate phases (cerussite, hydrozincite, smithsonite) in the

processed ores as well as with the well known high absorption capacity or even precipitation of metals by carbonates in calcareous soils.

The low mobility and bioavailability of Zn and Pb elements in the soils inside and outside the mining areas as well as in the river sediments is in agreement with the low content of both metal contaminants observed in surface water and groundwater samples. Contamination is restricted to the mining sites (tailings > coarse waste rocks > soils), while the samples collected outside do not show any evidence of contamination.

In the studied soils and wastes from the Upper Moulouya mining district, the low solubility of Zn and Pb mineral phases (anglesite, cerussite, galena; hemimorphite, hydrozincite, smithsonite, sphalerite, willemite) and the presence of a high proportion of carbonates (due to the limestone environment) largely affect the transfer of the metals, reducing their mobility by dissolution. The transfer might occur only by wind and water erosion of fine particles.

Zn and Pb are mostly found in the fine earth fraction which is more contaminated than the skeleton. In the majority of the samples, especially in the tailings, the clay fraction is enriched in metal contaminants, but its contribution to the total concentrations of metal contaminants in the fine earth is often negligible.

Only a multidisciplinary investigation in which methods provide complementary and converging data can lead to a comprehensive understanding of the history of industrial soil contaminations and to the identification of the forms and mobilities of metallic contaminants.

The need to reclaim abandoned mines to a high standard, particularly to meet pollution problems, is therefore even more critical now than in the past.

A range of reclamation techniques is available for metalliferous substrates but only through the use of vegetation to stabilize mine wastes can complete long-term rehabilitation be achieved. Successful revegetation can be a permanent and visually attractive solution and, at the same time, be relatively inexpensive. A vegetation cover can be effective in providing the necessary surface stability to prevent wind-blow of contaminated particulates, and in reducing water pollution by interception of a substantial proportion of incident precipitation.

Although revegetation is desirable, metalliferous wastes are very unfavorable environments for plants because the presence of many growth-limiting factors – particularly residual high levels of heavy metals, macronutrient deficiencies and poor substrate structure. Such features result in most metal wastes being largely devoid of any natural vegetation, even many years after abandonment. Consequently, experimentation has been undertaken at mine sites to attempt to elucidate and overcome limitations to vegetation establishment, allowing large-scale revegetation schemes to be formulated. Although such schemes have often been

successful at specific sites, their widespread application is limited owing to the great variation in physical, chemical and biological factors which exist between mine wastes (Tordoff, 2000). An alternative method for a restoration of abandoned mining sites is to consider them as historic heritage and, in this way, to protect them with different legal dispositions. Mining activities can be considered a special type of industrial site in that they encompass not only architectural but also landscape elements related to geology or topography. Nevertheless, these new economic potentials must be compatible with the obligation to maintain a low environmental risk in sites where the heavy metal concentrations are very high. A critical study based on cultural and environmental risks and economic values is needed in order to obtain a compromise between heritage conservation and the creation of new economic sources, without forgetting the role of the historic heritage in mining towns in keeping the local idiosyncrasy.

References

Abarro A., Bouchta R., Barodi E. B. (1998). Activité minière au Maroc. Chronique Minière Research & Exploration, 531–532, 3–8.

Abrahams P.W., Thornton I. (1987). Distribution and extent of land contaminated by arsenic and associated metals in mining regions of southwest England. Transactions of the Institution of Mining and Metallurgy, 96, B1-B8.

Adamo P., Arienzo M., Bianco M. R., Terribile F., Violante P. (2002). Heavy metal contamination of the soils used for stocking raw materials in the former ILVA iron-steel industrial plant of Bagnoli (southern Italy). The Science of the Total Environment 295, 17-34.

Adamo P., Denaix L., Terribile F., Zampella M. (2003). Characterization of heavy metals in contaminated volcanic soils of the Solofrana river valley (southern Italy). Geoderma, 2027, 1-25.

Adamo P., Dudka S., Wilson M.J., McHardy W.J. (1996). Chemical and mineralogical forms of Cu and Ni in contaminated soils from the Sudbury mining and smelting region, Canada. Environ. Pollut. 91 (1), 11-19.

Adamo P., Zampella M. (2008). Chemical speciation to assess potentially toxic metals (PTMs) bioavailability and geochemical forms in polluted soils. *In*: Environmental Geochemistry: Site Characterization, Data Analysis and Case Histories (De Vivo B., Belkin H. E., Lima A. Eds.), Elsevier, Amsterdam (The Netherlands), pp. 175-212.

Adriano D.C. (1986). Trace elements in the terrestrial environment. Berlin Heidelberg New York: Springer.

Agarkova M.G., Tselishcheva L.K., Stroganova M.N. (1991). Morphologic and genetic characteristics and systematics of urban soils. Moscow Univ. Soil Sci. Soc. Bull. 46(2): 12-16.

Ajmone-Marsan F., Biasioli M., Kralj T., Grčman H., Davidson C.M., Hursthouse A.S., Madrid L., Rodrigues S. (2008). Metals in particle-size fractions of the soils of five European cities. Environmental Pollution, 152, 73-81.

Allen H.E. (1997). Importance of speciation of metals in natural waters and soils to risk assessment. In: Report of International Workshop on Risk Assessment of Metals and their Inorganic Compounds. International Council on Metals and the Environment, Ottawa. pp. 141-157.

Alloway B.J. (1995). The origins of heavy metals in soils. In: Alloway B.J. (Ed.), Heavy Metals in Soils. Blackie Academic and Professional Publ., New York. 368 pp.

Alwan A.K. and Williams A. (1979). Mineral formation from aqueous solution. Part I. The deposition of hydrozincite, $Zn_5(OH)_6(CO_3)_2$, from natural waters. Transition Met. Chem.. 4, 128-132.

Amade E. (1965). Les gisements de plomb de Zeïda et de Bou-Mia. Notes & M. Serv. Géol. Maroc 181, 175-184.

Banks D., Younger P.L., Arnesen R.T., Iversen E.R., Banks S. (1997). Mine-water chemistry: the good, the bad and the ugly. Environ Geol, 32: 157–174.

Bell F.G., Bullock S.E.T., Hälbich T.F.J., Lindsay P. (2001). Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. International Journal of Coal Geology, 45, 195–216.

Bell F.G., Genske D.D. (2000). Restoration of derelict mining sites and mineral workings. Bull Eng Geol Env, 59: 173–185.

Bendahou Z. (1995). La zone littorale de la Moulouya (Maroc nord oriental) : transits sédimentaires, évolution morphologique, géochimiques et état de la pollution. Thèse de 3ème cycle. Université M^{ed} V, Rabat, 197 p.

Björlykke A., Sangster D.F. (1981). An overview of sandstone lead deposits and their relationship to red-bed copper and carbonate-hosted lead-zinc deposits. Econ Geol 75th Anniversary. 178-213.

Bolan N.S., Duraisamy V.P. (2003). Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. Aust. J. Soil Res., 41, 533-555.

Bouabdli A., Saidi N., M'Rabet S., Escarre J., Leblanc M. (2005). Oued Moulouya: vecteur de transport des métaux lourds (Maroc). Rev. Sci. Eau 18/2, 199-213.

Boularbah A., Schwartz C., Bitton G., Aboudrar W., Ouhammou A., Morel J.L. (2006b). Heavy metal contamination from mining sites in South Morocco: 2. Assessment of metal accumulation and toxicity in plants. Chemosphere, 63, 811–817.

Boularbah A., Schwartz C., Bitton G., Morel J.L. (2006a). Heavy metal contamination from mining sites in South Morocco: 1. Use of a biotest to assess metal toxicity of tailings and soils. Chemosphere, 63, 802–810.

Bowen H. (1979). Environmental Chemistry of the Elements. Academic Press, London. cited in Vymazal 1995.

Buondonno A. and Coppola E. (2005). Metodi di dissoluzione selettiva. Cap. VI in: Metodi di analisi mineralogica del suolo. 2005 (P. Adamo ed.). Ministero delle politiche agricole e forestali. Franco Angeli. Milano.

Buondonno C., Ermice A., Buondonno A., Murolo M., Pugliano L. (1998). Human-Influenced Soils from an Iron and Steel Works in Naples, Italy. Soil Sci Soc Am J, 62: 694-700.

Burghardt W. (1994a). Characteristics, classification and quality of urban and industrial soils of the Ruhr area, Germany. Proc. World Congress of Soil Science, 15th. Acapulco, Mexico, 10-16 July 1994. I.S.S.S. and the Mexican Society of Soil Science. 6b: 277-278.

Burghardt W. (1994b). Soils in urban and industrial environments. Z. Pflanzenernaehr. Bodenkd. 157: 205-214.

Callender E. (2003). Heavy metals in the environment-historical trends. Treatise on Geochemistry, vol. 9. Elsevier, 67-105.

Carlton-Smith C.H., Davis R.D. (1983). Heavy metal species and availability in water and sediments. Water Pollution Control, 82, 544–561.

Chipera S.J. and Bish D.L. (2002). FULLPAT: A full-pattern quantitative analysis program for X-ray powder diffraction using measured and calculated patterns. Journal of Applied Crystallography, 35, 744-749.

Chopin E.I.B., Black S., Hodson M.E., Coleman M.L., Alloway B.J. (2003). A preliminary investigation into mining and smelting impacts on trace elements concentrations in the soils and vegetation around Tharsis, SW Spain. Mineral. Mag. 67, 279-288.

Chronicle of mineral research and exploration (1998). In: B.R.G.M. (Eds.), pp. 531–532, 185 pp.

Cidu R., Biagini C., Fanfani L., La Ruffa G., Marras I. (2001). Mine closure at Monteponi (Italy): effect of the cessation of dewatering on the quality of shallow groundwater. Applied Geochemistry, 16, 489-502.

Cidu R., Biddau R., Fanfani L. (2009). Impact of past mining activity on the quality of groundwater in SW Sardinia (Italy). Journal of Geochemical Exploration 100, 125–132.

Ciolkosz E.J., Cronce R.C., Cunningham R.L., Petersens G.W. (1985). Characteristics, genesis and classification of Pennsylvania minesoils. Soil Sci. 139: 232-238.

Clark M.W., Walsh S.R., Smith J.V. (2001). The distribution of heavy metals in an abandoned mining area; a case study of Strauss Pit, the Drake mining area, Australia: implication for the environmental management of mine sites. Environmental Geology, 40 (6).

Dahlin C.L., Williamson C.A., Collins W.K., Dahlin D.C. (2002a). Part III – heavy metals: can standard sequential extraction determinations effectively define heavy metal species in Superfund site soils? Contaminated sìSoils 7, 87-114.

Dahlin C.L., Williamson C.A., Collins W.K., Dahlin D.C. (2002b). Sequential extraction versus comprehensive characterization of heavy metal species in brownfield soils. Environmental Forensics 3(2), 191-201.

D'Amore J.J., Al-Abed S.R., Scheckel K.G., Ryan J.A. (2005). Methods for Speciation of Metals in Soils: A Review. J. Environ. Qual., Vol. 34: 1707–1745.

Davis A., Drexler J.W., Ruby V., Nicholson A. (1993). Micromineralogy of mine wastes in relation to lead bioavailability. Butte, Montana. Environ. Sci. Technol. 27 : 1415-1425.

Derrar N. (1996). Synthèse géologique et hydrologique de la Haute et la Moyenne Moulouya (Maroc). Mémoire de fin d'études. Ecole Nationale de l'Industrie Minérale, Rabat, Maroc.

D.G.H. (2001). Etude du projet de construction du barrage Sidi Saïd. Direction Générale de l'Hydraulique, Ministère de l'équipement ; Royaume du Maroc, juillet 2001.

D.G.H. (2003). Direction Régionale de l'Hydraulique, Maroc. Projet de gestion des ressources en eau. Etude relative à la planification des ressources en eau du bassin de la Moulouya, juillet 2003.

Diack M., Stott D.E. (2001). Development of soil quality index for the Chalmers Silty clay Loam from the Midwest USA. In: Stott D.E., Mohtar R.H., Steinhardt G.C. (eds). The Global Farm. 10th. International Soil Conservation Organization Meeting, 550–555.

Direction de la Recherche et de la Planification de l'Eau (1994). Les grands barrages du Maroc. Publication de l'Administration de l'Hydraulique, Rabat, 80 pp.

D.M. (1990). Panorama de l'industrie minière, Tome 2. Direction des mines, Rabat, Maroc.

Drever J.I. (1973). The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter membrane peel technique. Am. Mineral., 58, 553-554.

D.R.H.M. (1996). Direction Régionale de l'Hydraulique de la Moulouya. Recueil des communications, journées de l'eau sous le thème : l'eau, l'environnement et le développement dans la région de l'oriental. Oijda, 27-28 juillet 1996.

Eberl D.D. (2003). User's guide to Rockjock - a program for determining quantitative mineralogy from powder X-ray diffraction data. US Geological Survey Open-File Report 03-78.

Eddebbi A., Saquaque A., Kersit M., Chbihi A. (1998). L'amas sulfuré de Hajar (Guemassa, Maroc). Chronique Minière Research & Exploration, 531–532, 45–54.

El Hachimi M.L. (2006). Les districts miniers Aouli-Mibladen-Zeida, abandonnés dans la Haute Moulouya (Maroc): potentiel de pollution et impact sur l'environnement. Thèse de Doctorat. Université IBN Tofail, Kénitra.

El Hachimi M.L., El Founti L., Bouabdli A., Saidi N., Fekhaoui M., Tassé N. (2006). Pb et As dans des eaux alcalines minières: contamination, comportement et risques (mine abandonnée de Zeïda, Maroc). Revue des sciences de l'eau, Volume 19.

El Jaouani L. (2001). Etude géologique et gitologique des gisements plombifères de la boutonnière d'Aouli (Aouli, Zeïda, Mibladen) Haute Moulouya (Maroc). Thèse de Doctorat. Université Med.V, Rabat.

El Khalil H., El Hamiani O., Bitton G., Ouazzani N., Boularbah A. (2008). Heavy metal contamination from mining sites in South Morocco: monitoring metal content and toxicity of soil runoff and groundwater. Environ Monit Assess, 136,147–160.

Emberger A. (1965a). Introduction à l'étude des minéralisations plombifères de la Haute Moulouya, Maroc. Colloque sur des gisements stratiformes de plomb, zinc et de manganèse du Maroc. Notes & M. Serv. Géol. Maroc. N° 181, pp. 205-244.

Emberger A. (1965b). Eléments pour une synthèse métallogénique du district plombifère de la Haute Moulouya. Notes & M. Serv. Géol. Maroc 181, 205-244.

Farrah H., Pickering W.F. (1977). Influence of clay-solute interactions of aqueous heavy metals ions levels. Water Air Soil Pollut.; 8: 189–197.

Farrah H., Pickering W.F. (1978). Extraction of heavy metal ions sorbed on clays. Water Air Soil Pollut.; 9: 491–498.

Felenc R., Lenoble J.P. (1965). Le gite de plomb de Mibladen. Notes & M. Serv. Géol. Maroc 181, 185-204.

Gandy C.J., Younger P.L. (2007). Predicting groundwater rebound in the South Yorkshire Coalfield, UK. Mine Water Environ. 26, 70–78.

Genske D.D., Thein J. (1994). Recycling derelict land. In: Carrier W.D. (ed) Proc 1st Int Congr on Environmental Geotechnics, Edmonton. Bi-Tech Publications, Richmond, British Columbia, pp 493–498.

Giuliano V., Pagnatelli F., Bornoroni L., Toro L., Abruzzese C. (2007). Toxic elements at a disused mine district: particle size distribution and total concentration in stream sediments and mine tailings. J. Hazard. Mater. 148, 409-418.

Grandjean P., Landrigan P.J. (2006). Developmental neurotoxicity of industrial chemicals. Lancet 368, 2167-2178.

Halla V.F. (1962). The free energy of the formation of dolomite from its carbonate components. Sedimentology, 1: 191-199.

Hamilton E.I. (2000). Environmental variables in a holistic evaluation of land contaminated by historic mine wastes: a study of multi-element mine wastes in West Devon, England using arsenic as an element of potential concern to human health. Sci. Total Environ., 249, 171-221.

Hartwell T.D., Handy R.W., Harrys B.S., Williams M.S., Gehlbach S.H. (1983). Heavy metal exposure in populations living around zinc and copper smelters. Arch. Environ. Health, 38(5), 284-295.

Hem J.D. (1985). Study and interpretation of the chemical characteristics of natural water (3rd ed.). U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Herreweghe S.V., Swennen R., Cappuyns V., Vandecasteele C. (2002). Chemical associations of heavy metals and metalloids in contaminated soils near former ore treatment plants: a differentiated approach with emphasis on pH_{stat}-leaching. Journal of Geochemical Exploration, 76, 113–138.

Hillier, S. (1999). Use of an air-brush to spray dry samples for X-ray powder diffraction. Clay Miner. 34, 127-135.

Hillier S. (2003). Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction (XRPD). Int. Assoc. Sedimentol. Spec. Publ. 34, 213-251.

Hillier S., Roe M.J., Geelhoed J.S., Fraser A.R., Farmer J.G., Paterson E. (2003). Role of quantitative mineralogical analysis in the investigation of sites contaminated by chromite ore processing residue. The Science of the Total Environment 308, 195-210.

Hillier S., Suzuki K., Cotter-Howells J. (2001). Quantitative determination of cerussite (lead carbonate) by X-ray powder diffraction and inferences for lead speciation and transport in stream sediments from a former lead mining area in Scotland. Applied Geochemistry 16, 597-608.

Hogfeldt E. (1982). Stability constants of metal-ion complexes, part A: Inorganic ligands. Oxford: Pergamon Press. 310 pp.

Holmgren G.C.S. (1967). A rapid citrate-dithionite extractable iron procedure. Soil Sci Soc Am Proc 31, 210-211.

Houba V.J.G., Lexmond T.M., Novozamsky I., van der Lee J.J. (1996). State of the art and future developments in soil analysis for bioavailability assessment. Sci. Tot. Environ. 178, 21-28.

Howie and Broadhurst (1958). Am. Min. 43, 1210-1213.

Huang K., Lin S. (2003). Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan, Chemosphere, 53: 1113–1121.

Hudson-Edwards K.A., Macklin M.G, Curtis C.D., Vaughan D.J. (1996). Processes of formation and distribution of Pb-, Zn-, Cd- and Cu-bearing minerals in the Tyne basin, northeast England: implications for metal-contaminated river systems. Environ. Sci. Technol. 30, 72-80.

ICDD (1998). International Centre for Diffraction Data, Powder Diffraction File sets 1-48, Pennsylvania, USA.

Jambor and Pouliot (1965). Canad. Mineral. 8, 385-389.

Jébrak M., Marcoux É., Nasloubi M., Zaharaoui M. (1998). From sandstone- to carbonate-hosted stratabound deposits: an isotope study of galena in the Upper-Moulouya District (Morocco). Mineralium Deposita, 33, 406-415.

Jenkins R., Snyder R.L. (1996). X-ray Powder Diffractometry. John Wiley and Sons, New York.

Johnson M.S., Cooke J.A., Stevenson J.K.W. (1994). Revegetation of metalliferous wastes and land after metal mining. In: Hester R.E., Harrison R.M., Mining and Its Environmental Impact. Royal Society of Chemistry, 164 pp.

Johnson R.H., Blowes D.W., Robertson W.D., Jambor J.L. (2000). The hydrogeochemistry of the nickel rim mine tailings impoundment, Sudbury, Ontario. J. Contam. Hydrol. 41, 49-80.

Jung M.C. (2001). Heavy metal contamination of soils and waters in and around the Imcheon Au–Ag mine, Korea. Appl. Geochem. 16, 1369–1375.

Jung M.C., Thornton I., Chon H.T. (2002). Arsenic, Sb and Bi contamination of soils, plants, waters and sediments in the vicinity of the Dalsung Cu-W mine in Korea. Science of the Total Environment, 295, 81–89.

Kabata-Pendias A., Pendias H. (2001). Trace Elements in Soils and Plants. CRC Press, London.

Kirpichtchikova T.A., Manceau A., Spadini L., Panfili F., Marcus MA., Jacquet T. (2006). Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. Geochimica and Cosmochimica Acta 70, 2163-2190.

Koeckritz T., Thoming J., Gleyzes C., Odegard K.E. (2001). Simplification of sequential extraction scheme to determine mobilisable heavy metal pool in soils. Acta Hydrochimica et Hydrobiologica 29(4), 197-205.

Kraemer S.M., Hering J.G. (2004). Biogeochemical controls on the mobility and bioavailability of metals in soils and groundwater. Aquatic Sciences, 66, 1–2.

Krishnamurti G.S.R., Naidu R. (2003). Solid-solution equilibria of cadmium in soils. Geoderma 113, 17– 30.

Krishnamurti G.S.R., Smith L.H., Naidu R. (2000). Method for assessing plant-available cadmium. Australian Journal of Soil Research, 38, 823–836.

Lahlou A. (1996). Environmental and socio-economic impacts of erosion and sedimentation in North Africa. In: Proc Symp Erosion and Sediment Yield: Global and Regional Perspectives, Exeter, July, Rep 236, pp 491–500.

Lake D.L., Kirk P.W.W., Lester J.N. (1984). Fractionation, characterization and speciation of heavy metal in sewage sludge and sludge-amended soils: a review. Journal of Environmental Quality 13, 175-183.

Li X., Coles B., Ramsay M.H., Thornton I. (1995). Sequential extraction of soils for multielement analysis by ICP-AES. Chem. Geol. 124, 109-123.

Liu W.X., Coveney R. M., Chen J. L. (2003). Environmental quality assessment on a river system polluted by mining activities. Applied Geochemistry, 18, 749–764.

Loeppert R.H., Suarez D.L. (1996). Carbonate and gypsum. In: Methods of Soil Analysis. Part 3, Chemical Methods (D.L. Sparks, Ed.) – SSSA Book Sereis n.5. ASA and SSSA, Madison, Wi., USA.

Magalhaes M.C.F. and Silva M.C. (2003). Stability of lead (II) arsenates. Monatsh Chem 134: 735-743.

Marqués M.J., Martínez-Conde E., Rovira J.V., Ordóñez S. (2001). Heavy metals pollution of aquatic ecosystems in the vicinity of a recently closed underground lead-zinc mine (Basque Country, Spain). Environmental Geology 40: 1125-1137.

McBride M.B. (1989). Reactions controlling heavy metals solubility in soils. Adv. Soil Sci.; 10: 1-57.

McLean J.E., Bledsoe B.E. (1992). Behavior of Metals in Soils, EPAGroundWater Issue EPA/540/S-92/018.

Merrington G., Alloway B.J. (1994). The transfer and fate of Cd, Cu and Zn from two historic metalliferous mine sites in the UK. Appl Geochem 9: 677-687.

Misra V., Jaffery F.N., Viswanathan P.N. (1994). Risk assessment of water pollutants. Environmental Monitoring and Assesstment, 29, 29–40.

Morgan J.J., Stumm W. (1995). Chemical processes in the environment, relevance of chemical speciation. In “Metals and Their Compounds in the Environment” (E. Merian, ed.). pp. 67-103. VCH, Weinheim.

Morin G., Ostergren J.D., Juillot F., Ildefonse P., Calas G., Brown Jr. G.E. (1999). XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: importance of the adsorption processes. Amer. Miner. 84, 420-434.

Munsell Color (2000). Munsell Soil Color Charts. Revised Washable Edition. Gretagmacbeth, New Windsor, NY.

NAS (National Academy of Sciences) (1992). Restoration of aquatic ecosystems. Science, technology and public policy. National Academy Press, Washington, DC.

Nasloubi M. (1993). Genèse et modélisation des minéralisations plombifères de la haute Moulouya (Maroc). Mémoire de maîtrise, Université du Québec à Montréal.

Navarro M.C., Pérez-Sirvent C., Martínez-Sánchez M.J., Vidal J., Tovar P.J., Bech J. (2008). Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. Journal of Geochemical Exploration 96, 183-193.

Ngadi M. (1995). Précipitations et écoulements dans le bassin versant de la Moulouya (Maroc). Thèse de Doctorat Université Montpellier III, France, 333 p.

Ngiam L., Lim P. (2001). Speciation patterns of heavy metals in tropical estuarine anoxic and oxidized sediments by different sequential extraction schemes. The Science of the Environment 275, 53-61.

Nirel P.M.V., Morel F.M.M. (1990). Pitfalls of sequential extractions. Water Research 24, 1055-1056.

Novozamsky J., Lexmond T.M., Houba V.J.G. (1993). A single extraction procedure of soil for evaluation of uptake of some heavy metals by plants. International Journal of Environmental Analytical Chemistry 51, 47-58.

Omotoso O., McCarty D.K., Hillier S., Kleeberg R. (2006). Some successful approaches to quantitative mineral analysis as revealed by the 3rd Reynolds cup contest. Clays and Clay Minerals, Vol. 54, N°. 6, 748–760.

Osher L.J., Leclerc L., Wiersma G.B., Hess C.T., Guiseppe V.E. (2006). Heavy metal contamination from historic mining in upland soil and estuarine sediments of Egypt Bay, Maine, USA. Estuarine, Coastal and Shelf Science, 70, 169-179.

Pagnanelli F., Moscardini E., Giuliano V., Toro L. (2004). Sequential extraction of heavy metals in river sediments o fan abandoned pyrite mining area: pollution detection and affinity series. Environmental Pollution, 132, 189-201.

Passariello B., Giuliano V., Quaresima S., Barbaro M., Caroli S., Forte G., Carelli G., Iavicoli I. (2002). Evaluation of the environmental contamination at an abandoned mining site. Microchemical journal, 73, 245-250.

Patnaik and Pradyot (2003). Handbook of inorganic chemicals. McGraw-Hill.

Petris E. (1963). La laverie du gîte plombifère stratiforme de Mibladen, Mines et Géologie. Direction des mines, Rabat, Maroc. N° 21-22, 121-125.

Piqué A., Michard A. (1989). Moroccan hercynides: a synopsis. The Paleozoic sedimentary and tectonic evolution at the northern margin of West Africa, American Journal of Science. 289, pp. 286–330.

Querol X., Alastuey A., Lòpez-Soler A., Plana F. (2000). Levels and chemistry of atmospheric particulates induced by a spill of heavy metal mining wastes in the Doñana area, Southwest Spain. Atmos. Environ. 34, 239-253.

Rajlich P.M. (1983). Geology of Oued Mekta, a Mississipi Valley-type deposit, Touissit-Bou Beker region, eastern Morocco. Econ. Geol., 78, 1239-1254.

Ray S., Gault H.R., Dodd G. (1957). The separation of clay minerals from carbonate rocks. American Mineralogist, 42, 681–685.

Razo I., Carrizales L., Castro J., Díaz Barriga F., Monroy M. (2004). Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water Air Soil Pollut. 152, 129-152.

Rendell P.S., Batley G.E., Camerun A.J. (1980). Adsorption as a control of metal concentrations in sediment extracts. Environmental Science and Technology 14, 314-318.

Renella G., Adamo P., Bianco M.R., Landi L., Violante P., Nannipieri P. (2004). Availability and speciation of cadmium added to a calcareous soil under various managements. European Journal of Soil Science 55, pp. 123-133.

Ritchie G.S.P., Sposito G. (2002). Speciation in soils. In “Chemical Speciation in the Environment” (Ure A., Davidson C.M., eds.), pp. 237-264. Blackwell, Oxford.

Sahuquillo A., Lopez-Sanchez J.F., Rubio R., Rauret G., Thomas R.P., Davidson C.M., Ure A.M. (1999). Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. Anal. Chim. Acta 382, 317–327.

Saïdi N., Brhada F., Zaïd A., Bouabdli A., Escarré J. (2002). Impact de la mine d’Aouli sur l’écosystème au niveau de la Haute Moulouya (Maroc). Bull. Soc. Hist. nat. Toulouse, 138, 21-27.

Santillan-Medrano J, Jurinak JJ. (1975). The chemistry of lead and cadmium in soils: solid phase formation. Soil Sci. Soc. Am. Proc.; 39: 851–856.

Saunier A. (1963). La laverie du gîte plombifère filonien d'Aouli, Mines et Géologie. Direction des mines, Rabat, Maroc. N° 21-22, pp. 115-119.

Schmiermund R.L., Drozd M.A. (1997). Acid mine drainage and other mining influenced waters (MIW). In: Marcus J.J. (ed), Mining environmental handbook. ICP, London, pp 599–617.

Schmitt J.M. (1976). Sédimentation, paléoaltération, géochimie et minéralisation en plomb de la série Triasique de Zeïda (Haute Moulouya, Maroc). Thèse de Doctorat. Ecole nationale supérieure des mines, Paris.

Schön A. (1995). The forms and behaviour of heavy metals in soils from a former lead mining area in south west Scotland. MSc thesis, University of Aberdeen, UK.

Schulze D.G. (1986). Correction of mismatches in 2θ scales during differential X-ray diffraction. Clays and Clay Minerals, 34, 681-685.

Schwertmann S. (1964). The differentiation of iron oxide in soils by a photochemical extraction with acid ammonium oxalate. Zeitschrift für Pflanzenernährung, Düngung und Bodenkunde 105, 194-201.

Selim H.M., Sparks D.L (2001). Heavy metals release in soils. Boca Raton, Florida: CRC Press.

Shallari S., Schwartz C., Hasko A., Morel J.L. (1998). Heavy metals in soils and plants of serpentine and industrial sites of Albania. Sci. Tot. Environ. 209, 133–142.

Siebe C., Jahn R., Stahr K. (1996). Manual para la descripción y evaluación ecológica de suelos en el campo. Publicación Especial 4, Sociedad Mexicana de la Ciencia del Suelo, A.C., Chapingo, México.

Siegel F.R. (2002). Environmental Geochemistry of Potentially Toxic Metals. Springer.

Snoussi M., Haïda S., Imassi S. (2002). Effects of the construction of dams on the water and sediment fluxes of the Moulouya and the Sebou Rivers, Morocco. Reg. Environ. Change, 3:5–12.

Song Y., Wilson M.J., Moon H.S., Bacon J.R., Bain D.C. (1998). Chemical and mineralogical forms of lead, zinc and cadmium in particle size fractions of some wastes, sediments and soils in Korea. Applied Geochemistry, 14, 621-633.

Sposito G. (1984). The surface chemistry of soils. New York: Oxford University Press.

Stamatiadis S., Doran J.W., Kettler T. (1999). Field and laboratory evaluation of soil quality changes resulting from injection of liquid sewage sludge. Applied Soil Ecology, 12: 263–272.

Stewart B.A. (1992). Advances in Soil Science 20, I Sping-Verlag, New York, N.Y.

Strain M.R., Evans C.V. (1994). Map unit development for sand- and gravel-pit soils in New Hampshire. Soil Sci. Soc. Am. J. 58: 147-155.

Swanson and Fuyat (1953). NBS Circular 539, vol. III.

Tahiri M., Benyaïch F., Bounakhla M., Bilal E., Gruffat J.J., Moutte J. (2005). Multivariate analysis of heavy metal contents in soils, sediments and water in the region of Meknes (central Morocco). Environmental Monitoring Assessment, 102, 405–417.

Taylor J.C. (1991). Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. Powder Diff. 6, 2-9.

Tessier A., Campbell P.G.X., Bisson M. (1979). Sequential extraction procedure for the speciation of particular trace metals. Analytical Chemistry, 51, 844–850.

Thurman N.C., Sencindiver J.C. (1986). Properties, classification and interpretation of minesoils at two sites in West Virginia. Soil Sci. Soc. Am. J. 50: 181-185.

Tordoff G.M., Baker A.J.M., Willis A.J. (2000). Current approaches to the revegetation and reclamation of metalliferous mine wastes. Chemosphere, 41, 219-228.

Ure A.M., Davidson C.M. (1995). Chemical Speciation in the Environment. Blackie, Glasgow (pp. 408).

Ure A.M., Davidson C.M. (2002). Chemical speciation in soils and related materials by selective chemical extraction. In: Ure, A.M., Davidson, C.M. (Eds.), Chemical Speciation in the Environment. Blackwell Science, Oxford. pp. 265-300.

Ure A.M., Quevauviller Ph., Muntau H., Griepink B. (1993). Speciation of heavy metal in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. Internat.J. Environ. Anal. Chem. 51, 135–151.

USDA, 2005. Global Soil Regions map (http://soils.usda.gov/use/worldsoils/mapindex/order.html)

van Geen, Takesue R., Chase Z. (1999). Acid mine tailings in southern Spain. Sci. Total Environ. 242, 221-229.

Van Tonder G.J., Usher B.H., Dennis I., Vermeulen P.D. (2007). Predicting rebound in a deep collier in South Africa. Mine Water Environ. 26 (2), 79–87.

Vaughan D.J. and Craig J.R. (1978). Mineral chemistry of metal sulfides. Cambridge University Press, Cambridge.

Venditti D., Berthelin J., Durécu S., (2000b). A multidisciplinary approach to assess history, environmental risks, and remediation feasibility of soils contaminated by metallurgical activities. Part B: Direct metal speciation in the solid phase Archives of Environmental Contamination and Toxicology 38, 421-427.

Venditti D., Durécu S., Berthelin J., (2000a). A multidisciplinary approach to assess history, environmental risks, and remediation feasibility of soils contaminated by metallurgical activities. Part A: Chemical and physical properties of metals and leaching ability Archives of Environmental Contamination and Toxicology 38, 411-420.

Wadjinni A. (1998). Le plomb au Maroc: Cas des districts de Touissit et de Jbel Aouam. Chronique de la recherche minière, 531/532: 9-28.

Walkley A., Black I.A. (1934). An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. Soil Sci. 63: 251-263.

Weisz M., Polyák K., Hlavay J. (2000). Fractionation of elements in sediment samples collected in rivers and harbors at lake Balaton and its catchment area. Microchem. J. 67, 207–217.

Wennrich R., Mattusch J., Morgenstern P., Freyer K., Treutler H.C., Stärk H.J., Brüggemann L., Paschke A., Daus B., Weiss H. (2004). Characterization of sediments in an abandoned mining area; a case study of Mansfeld region, Germany. Environmental Geology, 45: 818–833.

WHO (2008). Guidelines for drinking-water quality: incorporating 1st and 2nd addenda, Vol.1, Recommendations. – 3rd ed.

Wilson M.J. (1987). A handbook of determinative methods in clay mineralogy. Blackie & Son, New York.

Winburn R.S., Lerach S.L., Jarabek B.R., Wisdom M.A., Grier D.G., McCarthy J. (2000). Quantitative XRD analysis of coal combustion by-products by the Rietveld method. Testing with standard mixtures. Adv X-Ray Anal; 42: 387 –395.

Yu K.C., Tsai L.J., Chen S.H., Ho S.T. (2001). Correlation analyses binding behavior of heavy metals with sediment matrices. Water Res. 35, 2417–2428.

Zevin L.S., Kimmel G. (1995). Quantitative X-ray Diffractometry. Springer-Verlag, New York.

CARTE DU MAROC 1/100 000

ميدلت
MIDELT

FEUILLE NI-30-II-3

Sampling Points

Metamorphic schist

Granite

Permian-Triassic Arkose

Middle-Liassic Dolostone

Pb ores - Stratabound

Dressé, dessiné et publié par la Division de la Carte en 1968
Reproduction interdite.

Levés stéréotopographiques aériens de 1962. (Restitution à l'appareil Poivilliers-S.O.M.).
Non compilétés sur le terrain.

Nivellement général du Maroc.

L'équidistance des courbes est de 50 mètres.

Ellipsoïde de Clarke 1880 Système géodésique Merchich.
Projection conique conforme de Lambert Nord-Maroc.

Echelle 1/100 000

Dressé, dessiné et publié en 1993 par la Direction de la Conservation Foncière, du Cadastre et de la Cartographie
Division de la Catographie

Figure 2.1. Location of sampling points.

1703

ميدلت
MIDELT

CARTE DU MAROC 1/100 000

FEUILLE NI-30-II-3

Sampling Points — Groundwater / Surface water

Metamorphic schist

Granite

Permian-Triassic Arkose

Middle-Liassic Dolostone

Pb ores - Stratabound

Dressé, dessiné et publié par la Division de la Carte en 1968
Reproduction interdite.

Levés stéréotopographiques aériens de 1962. (Restitution à l'appareil Poivilliers-S.O.M.).
Non complétés sur le terrain.

Nivellement général du Maroc.

L'équidistance des courbes est de 50 mètres.

Ellipsoïde de Clarke 1880 Système géodésique Merchich.
Projection conique conforme de Lambert Nord-Maroc.

Echelle 1/100 000

Kilomètre 1 0 1 2 3 4 5 6 7 8 9 10 Kilomètres

DIVISIONS ADMINISTRATIVES

TABLEAU SYNOPTIQUE DES FEUILLES

La déclinaison magnétique correspond au centre de la feuille et au 1er Janvier 1956.

La déclinaison magnétique diminue chaque année de 14 minutes centésimales.

Bois — Broussaille — Jardins — Plantation

Dressé, dessiné et publié en 1993 par la Direction de la Conservation Foncière, du Cadastre et de la Cartographie
Division de la Cartographie

Figure 3.1. Location of sampling points.